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Pseudoternary System Calcium Oxide-Monocalcium Aluminate ($CaO \cdot Al_2O_3$)-Dicalcium Ferrite ($2CaO \cdot Fe_2O_3$)

Terry F. Newkirk [1, 2] and R. D. Thwaite [2]

The system CaO-$CaO \cdot Al_2O_3$-$2CaO \cdot Fe_2O_3$ is of importance to portland cement chemistry because it provides information on the composition of the iron-bearing phase in cement clinker.

Iron-bearing solid solutions in the system were found to exist as a continuous narrow band extending from $2CaO \cdot Fe_2O_3$ to $6.45CaO \cdot 2.31Al_2O_3 \cdot F_2O_3$. Additional tie lines were established to show the composition of the iron-bearing solid solution phase (Fss) and liquid phases during the course of crystallization of mixtures within the system. Isotherms have been located for the regions of principal interest. Compatibility relations differ somewhat from those reported by previous investigators. The composition of the iron-bearing phase in equilibrium with CaO and $3CaO \cdot Al_2O_3$ at the ternary invariant point proved to be lower in Fe_2O_3 than that reported by Swayze. Other results are in general agreement with the work of Swayze and of Yamauchi.

1. Introduction

In its effect on the constitution of portland cement clinker, Fe_2O_3 is next in importance to the three principal components CaO, Al_2O_3, and SiO_2. Le Chatelier [1][3] postulated the existence in portland cement clinker of a ternary compound of calcium, aluminum, and ferric oxides having a possible formula $3CaO \cdot Al_2O_3 \cdot Fe_2O_3$. In their pioneering work on the system CaO-$CaO \cdot Al_2O_3$-$CaO \cdot Fe_2O_3$, Hansen, Brownmiller, and Bogue [2] discovered a continuous series of solid solutions between the compound $2CaO \cdot Fe_2O_3$ and what appeared to be a compound, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The latter phase ($Al_2O_3/Fe_2O_3$ weight ratio 0.64) was believed to constitute the end of the solid-solution series. Commercial portland cements are ordinarily of higher Al_2O_3/Fe_2O_3 ratios than 0.64. The existence of a series of solid solutions in the region of lower ratios was, therefore, not of primary interest to portland cement chemists at that time, because it appeared that the iron-bearing solid solutions would rarely, if ever, be found in clinker.

Based on this earlier work, Lea and Parker [3] investigated the system CaO-$2CaO \cdot SiO_2$-$5CaO \cdot 3Al_2O_3$ [4]-$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, treating all of the calcium aluminoferrite phases as having the composition $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

Further work on the ternary system CaO-$CaO \cdot Al_2O_3$-$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ was done by McMurdie [6] who studied in detail the extent of solid solutions within that system. His compositions and two of the temperatures for the ternary invariant points differ from those reported [2] earlier. Certain discrepancies noted between the calculated and observed compositions of the iron-bearing phase in some commercial clinkers led to independent investigations by Yamauchi [7] and by Swayze [8] of the system CaO-$5CaO \cdot 3Al_2O_3$-$2CaO \cdot Fe_2O_3$ and by Swayze [9] of the quaternary system CaO-$5CaO \cdot 3Al_2O_3$-$2CaO \cdot Fe_2O_3$-$2CaO \cdot SiO_2$ and of the same system as modified by 5 percent of MgO. These investigators discovered that the solid solution between $2CaO \cdot Fe_2O_3$ and a hypothetical $2CaO \cdot Al_2O_3$ extended beyond $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, in which the molar Al_2O_3/Fe_2O_3 ratio is unity. This discovery was of importance to the cement industry because it showed that the composition of the principal iron-bearing phase in most commercial clinkers is not fixed but may vary with the chemical composition of the clinker. Changes in the compositions of these iron-bearing solid solutions can affect significantly the constitution and properties of the clinker. Swayze [8, 9] reported that the solid solutions of interest are confined to the pseudoternary system CaO-$5CaO \cdot 3Al_2O_3$-$2CaO \cdot Fe_2O_3$. His diagram for the ternary system differed in a number of respects from those of the earlier investigators.

Although the extension of the iron-bearing solid-solution series in the ternary system to higher Al_2O_3/Fe_2O_3 ratios than $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ has been confirmed by several investigators, there is some disagreement among them as to the limits of this series. Swayze placed the high-Al_2O_3 limit at the composition $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ (molar Al_2O_3/Fe_2O_3 ratio of 2.0) whereas Yamauchi [7] and Malquori and Cirilli [10] placed it at a ratio of 2.2 and 2.3, respectively.

Solid solution was pictured by Swayze as being limited to a straight line extending from $2CaO \cdot Fe_2O_3$ to the composition $6\,CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ in the ternary system. Yamauchi referred to the solid solution series as being confined to a "swelled straight line." The composition $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is a solid solution on this line [7, 10]. Some solid solution departing from the line is also indicated in the data of McMurdie [6] who noted that $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ can

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[2] Research Associate, Portland Cement Association Fellowship, National Bureau of Standards.
[3] Figures in brackets indicate the literature references at the end of this paper.
[4] Studies by Büssem and Eitel [4], and by Thorvaldson and Schneider [5], indicate that the correct formula for this compound is $12CaO \cdot 7Al_2O_3$. The latter formula is used in the present work except in references to the work of earlier authors.

take into solution up to 5 percent of $3CaO \cdot Al_2O_3$, $5CaO \cdot 3Al_2O_3$, or $CaO \cdot Al_2O_3$.

Because the composition of the iron-bearing phase is variable, it is necessary for the investigator to depict on the phase diagram the changing composition of these crystals as crystallization (or melting) proceeds by means of tie lines or conodes. Two tie lines were given by Swayze in each of the diagrams representing the ternary, quaternary, and quinary systems. The number is not sufficient, however, to permit one to follow the course of crystallization within each system.

The present study was undertaken in order to reconcile differences in published data on the ternary system. It also has the purpose of obtaining additional information on the system, especially the establishment of a sufficient number of tie lines to permit computation of the approximate composition of the calcium aluminoferrite phase throughout the crystallization of mixtures within the system. This information has an important bearing on the constitution of portland cement.

2. Experimental Methods

2.1. Preparation of Mixtures

All compositions were synthesized from reagent grade calcium carbonate S. L. (low-alkali type), Fe_2O_3, and Linde type-B alumina (99.9% Al_2O_3). These materials were dried and then weighed in the correct amounts to give 10-g samples on ignition. After an initial mixing for several hours in glass jars, the mixtures were ground in an alumina mortar to pass a No. 325 sieve. Each mixture was heated for three periods of at least 2 hr in the range 1,100° to 1,310° C before being studied. Following each burn, the sample was ground, screened, and remixed. Composition gradients within the individual crystals, because of changes in the liquid composition during crystallization, were unlikely because the temperature of first liquid formation for nearly all mixtures studied was above 1,310°. The exceptions, five mixtures with compositions in the $CaO \cdot Fe_2O_3$ compatibility regions, were heated 15 hr or more at 1,180° C to insure homogeneity. These mixtures were used for quenching experiments and for differential thermal analysis. Further heat treatment was given selected compositions prior to examination by X-ray diffraction methods.

2.2. Temperature Measurement and Control

Temperatures in the furnace were measured with a platinum–platinum-10%-rhodium thermocouple calibrated at melting points defined as follows: $CaMgSi_2O_6$, 1,392° C and $BaO \cdot 2SiO_2$, 1,418° C. The furnace was maintained at constant temperature within ±0.5° C by means of a controller of the type developed by Mauer [11].

2.3. Methods of Investigation

Phase relations in this system were investigated by differential thermal analysis (DTA) and the standard quenching technique. The DTA studies made use of a pellet method [12] developed in the Fellowship laboratory. In the quenching technique, presintered mixtures of oxides were held in platinum envelopes at constant temperature for 2 hr until equilibrium was reached between solid and liquid phases, and then quenched in water. The identification of phases was based on the results of microscopic examinations and X-ray powder diffraction patterns made with a Philips high-angle diffractometer using $CuK\alpha$ radiation.

For studying final products of crystallization, small quantities of 17 glasses with compositions in the vicinity of the iron-bearing solid solution region, and near invariant points, were collected by quenching from above the liquidus. After devitrification in platinum capsules at 1,300° C for approximately 40 hr, the charges were removed from the furnace and mixed by grinding in a boron carbide mortar. This procedure was used to insure attaining equilibrium among the solid phases. A portion of each sample was then mixed with 5 percent by weight of pure tungsten powder as an internal standard prior to X-ray powder diffraction study. The diffraction patterns showed that all samples were well crystallized as a result of their heat treatment. The important portions of each pattern were scanned at a speed of 1/8°/min over the range 15° to 110° (2θ) using a 0.003-in. receiving slit, and a time constant that was small as compared with the time width [13] of the slit.

Tie lines in the system were determined by microscopic study and X-ray powder patterns of selected mixtures. Chosen compositions in the primary-phase region for the calcium aluminoferrite solid solution (Fss) were quenched at a temperature about 1° C below that at which the secondary crystalline phase appears, after being held long enough to reach equilibrium. By measuring d_{hkl} for a series of peaks found in the patterns, and correlating these with d_{hkl} values determined for the solid-solution series, the composition of the solid solution in equilibrium with the liquid and the secondary phase was determined. The tie line through points in the phase diagram representing the original mixture and the solid-solution phase intersects the boundary of the Fss primary-phase region at the liquidus temperature corresponding to the appearance of the secondary phase in crystallization of the original mixture.

3. Results and Discussion

3.1. General Information on the System

The phase diagram for the condensed ternary system CaO-$CaO \cdot Al_2O_3$-$2CaO \cdot Fe_2O_3$ developed in the present investigation appears as figure 1. The diagram contains a considerable amount of new information on tie lines, isotherms, compatibility regions, and the extent of the calcium aluminoferrite solid solutions in the system. The binary invariant points for CaO-C_3A, C_3A-$C_{12}A_7$, and $C_{12}A_7$-CA were determined by Rankin and Wright [15], and that for CaO-C_2F by Swayze [8]. Experimental data on which the diagram is based are given in table 1.

FIGURE 1

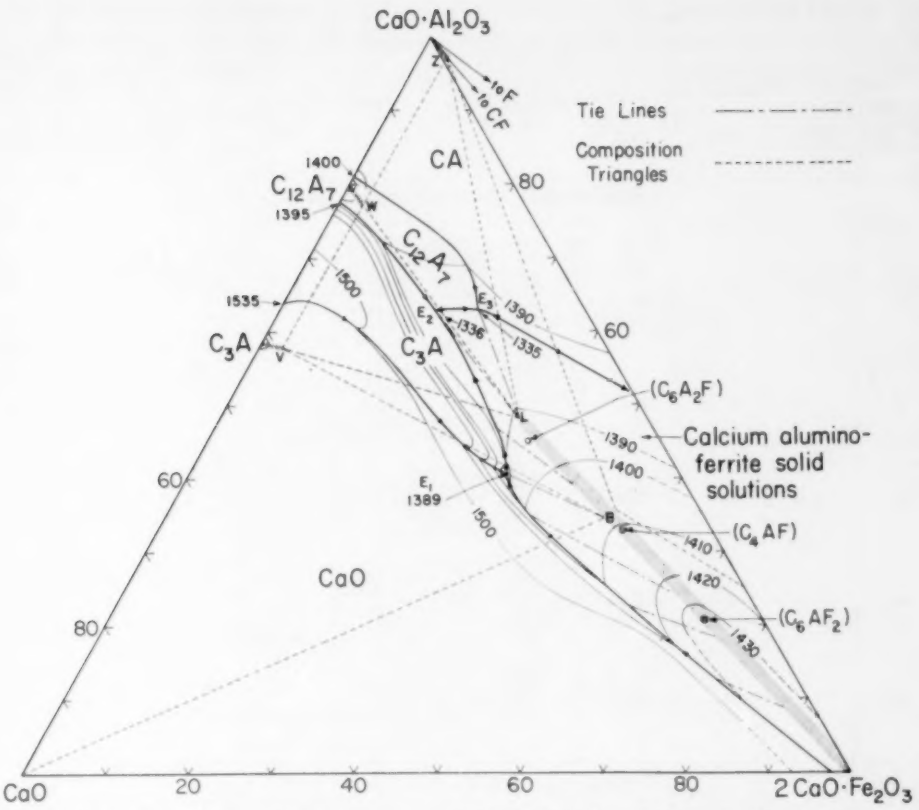

FIGURE 1. *Equilibrium diagram of the pseudo-ternary system* CaO-CaO·Al_2O_3-2CaO·Fe_2O_3 *showing isotherms, tie lines, and the fields of the primary crystalline phases.*

TABLE 1. *Quenching and DTA data for mixtures in the system* CaO–CaO·Al_2O_3–2CaO·Fe_2O_3

Mixture No.	Composition (Weight percent)			Quenching temperature	Phases present	Observed temperature of phase changes (DTA)	
	CaO	CA	C_2F			First liquid formation	Other phase changes
Mixtures having CaO·Al_2O_3 as primary phase							
				°C		°C	°C
73	16	79	5	1,428	All glass	----	----
				1,425	Glass+rare CA	----	----
				1,411	Glass+some CA	----	----
				1,401	Glass+CA+much $C_{12}A_7$	----	----
74	12	75	13	1,429	All glass	----	----
				1,427	Glass+a little CA	----	----
				1,403	Glass+CA+much $C_{12}A_7$	----	----
72	2	59	39	1,395	All glass	----	----
				1,390	Glass+very rare CA	----	----
				1,389	Class+some CA	----	----
70	3	56	41	1,361	All glass	----	----
				1,358	(CA liquidus)	----	----
				1,356	Glass+trace of CA	----	----
				1,352	Glass+moderate amount of CA	----	----
				1,331	Not sintered; CA+Fss+trace $C_{12}A_7$	----	----
68	9.56	65.17	25.27	1,375	(CA liquidus)	1,335	----
				1,370	Glass+very rare CA		
				1,365	Glass+trace CA		
				1,357	Glass+small amount of CA		
64	7.35	62.01	30.64	1,402	All glass	1,345	----
				1,396	(CA liquidus)		
				1,395	Glass+very rate CA		
				1,390	Glass+CA		
				1,355	Glass+much CA		
				1,350	(Fss phase appears)		
				1,348	Glass+much CA+rare Fss		

TABLE 1. *Quenching and DTA data for mixtures in the system* $CaO–CaO·Al_2O_3—2CaO·Fe_2O_3$—Continued

Mixture No.	Composition (Weight percent)			Quenching temperature	Phases present	Observed temperature of phase changes (DTA)	
	CaO	CA	C_2F			First liquid formation	Other phase changes
Mixtures having $12CaO·7Al_2O_3$ as primary phase							
52	18.99	67.01	14	1,377	All glass		
				1,376	($C_{12}A_7$ liquidus)		
				1,375	Glass+rare $C_{12}A_7$		
				1,356	Glass+moderate amount of $C_{12}A_7$		
					Index of $C_{12}A_7$=1.614±0.004		
				1,338	Glass+much $C_{12}A_7$		
				1,335	Not sintered in packet		
60	11.59	69.41	19.0	1,393	($C_{12}A_7$ liquidus)	1,333	
				1,391	Mostly glass+rare $C_{12}A_7$		
				1,389	(CA appears as second phase)		
				1,387	Glass+$C_{12}A_7$+rare CA		
				1,338	Glass+$C_{12}A_7$+CA+Fss		
54	13.19	67.81	19.0	1,351	All glass		
				1,349	($C_{12}A_7$ liquidus)		
				1,346	Glass+very rare $C_{12}A_7$		
				1,336	Glass+$C_{12}A_7$+Fss		
				1,333	Not melted		
67	11.99	67.61	20.40	1,352	All glass	1,335	
				1,351	($C_{12}A_7$ liquidus)		
				1,349	Glass+rare $C_{12}A_7$		
				1,336	Glass+$C_{12}A_7$+CA+Fss		
				1,334	First liquid		
				1,333	Not sintered; $C_{12}A_7$+CA+Fss		
69	13	64	23	1,358	All glass		
				1,357	($C_{12}A_7$ liquidus)		
				1,356	Glass+trace $C_{12}A_7$		
				1,342	Glass+$C_{12}A_7$+Fss+trace CA+quench growths.		
Mixtures having $3CaO·Al_2O_3$ as primary phase							
43	24.89	70.11	5.00	1,466	Estimated C_3A liquidus	1,338	
				1,465	Glass+rare C_3A		
				1,460	Glass+some C_3A		
				1,381	Glass+C_3A		
				1,377	($C_{12}A_7$ appears as second phase)		
				1,375	Glass+C_3A+trace $C_{12}A_7$		
44	20.81	74.19	5.0	1,402	All glass		
				1,400	(C_3A liquidus)		
				1,399	Glass+small amount of C_3A		
				1,395	Glass+C_3A		
				1,394	($C_{12}A_7$ appears as second phase)		
				1,392	Glass+C_3A+$C_{12}A_7$		
45	20.59	69.41	10	1,405	All glass		
				1,401	(C_3A liquidus)		
				1,400	Glass+rare C_3A		
				1,379	Glass+C_3A		
					Index C_3A=1.715±0.002		
				1,375	($C_{12}A_7$ appears as second phase)		
				1,372	Glass+C_3A+very rare $C_{12}A_7$		
9	23.57	66.43	10	1,356	Glass+C_3A	1,333	
				1,352	($C_{12}A_7$ appears as second phase)		
				1,348	Glass+C_3A+much $C_{12}A_7$		
13	22.26	62.74	15	1,353	Glass+lots of C_3A	1,335	
				1,352	Glass+C_3A+some $C_{12}A_7$		
				1,344	Glass+much C_3A+much $C_{12}A_7$		
53	18.49	62.78	18.73	1,366	All glass		
				1,365	(C_3A liquidus)		
				1,364	Glass+rare C_3A		
				1,348	Glass+C_3A		
				1,347	($C_{12}A_7$ appears as second phase)		
				1,346	Glass+C_3A+$C_{12}A_7$+quench growths		
46	19.37	60.63	20	1,384	All glass		
				1,383	(C_3A liquidus)		
				1,381	Glass+rare C_3A		
				1,356	Glass+moderate amount C_3A		
				1,355	(Fss appears as second phase)		
				1,354	Glass+C_3A+a few Fss crystals		
8	20.95	59.05	20	1,392	All glass	1,338	1,353
				1,390	(C_3A liquidus)		
				1,388	Glass+C_3A+quench growths		
				1,355	Glass+C_3A+Fss+quench growths		
61	29.77	62.23	8	1,515	All glass		
				1,514	C_3A+glass		
				1,512	Glass+much C_3A		

TABLE 1. *Quenching and DTA data for mixtures in the system* $CaO–CaO·Al_2O_3–2CaO·Fe_2O_3$—Continued

Mixture No.	Composition (Weight percent)			Quenching temperature	Phases present	Observed temperature of phase changes (DTA)	
	CaO	CA	C_2F			First liquid formation	Other phase changes
Mixtures having $3CaO·Al_2O_3$ as primary phase							
62	26.56	57.44	16	1,486	All glass	1,339	1,344
				1,483	(C_3A liquidus)		
				1,481	Glass+a few C_3A crystals		
				1,375	Glass+much C_3A		
				1,373	(Fss appears as second phase)		
				1,371	Glass+C_3A+very rare Fss		
14	19.65	55.35	25	1,384	All glass	-----	-----
				1,382	(C_3A liquidus)	-----	-----
				1,380	Trace C_3A+glass	-----	-----
				1,366	Fss+C_3A+glass	-----	-----
57	18.36	56.64	25	1,384	All glass	-----	-----
				1,382	(C_3A liquidus)	-----	-----
				1,380	Glass+rare C_3A	-----	-----
				1,372	Glass+rare C_3A	-----	-----
				1,371	(Fss appears as second phase)	-----	-----
				1,370	Glass+rare C_3A+Fss	-----	-----
63	23.74	50.26	26.0	1,444	All glass	-----	-----
				1,442	(C_3A liquidus)	-----	-----
				1,440	Glass+trace of C_3A	-----	-----
				1,387	Glass+much C_3A	-----	-----
				1,385	(Fss appears as second phase)	-----	-----
				1,383	Glass+much C_3A+some Fss	-----	-----
47	18.94	51.06	30	1,383	All glass	-----	-----
				1,382	(C_3A liquidus)	-----	-----
				1,378	Glass+small amount C_3A	-----	-----
				1,377	(Fss appears as second phase)	-----	-----
				1,370	Glass+C_3A+Fss+quench growths	-----	-----
24	25.10	46.90	28	1,439	All glass	1,389	-----
				1,439	(C_3A—CaO liquidus)		
				1,438	Trace CaO+trace C_3A+glass		
				1,436	C_3A+glass+few quench growths		
65	19.6	46.4	34	1,394	All glass	1,369	1,381
				1,392	(C_3A liquidus)		
				1,390	Glass+rare C_3A+quench growth		
				1,387	Glass+rare C_3A		
				1,385	(Fss appears as second phase)		
				1,384	Glass+C_3A+Fss		
66	20	44.3	35.7	1,391	All glass	1,388	-----
				1,390	(C_3A liquidus)		
				1,389	Glass+rare C_3A		
				1,387	Glass+rare C_3A		
				1,386	(Fss appears as second phase)		
				1,384	Glass+C_3A+Fss		
28	20.77	42.60	36.63	1,402	All glass	1,389	-----
				1,395	Glass+quench growths		
				1,392	(C_3A liquidus)		
				1,389	Glass+a little C_3A+Fss+quench growths.		
Mixtures having CaO as primary phase							
21	35.92	63.08	1	1,611	CaO in glass. Liquidus not determined.	-----	-----
				1,525	Glass+CaO	-----	-----
				1,522	(C_3A appears as second phase)	-----	-----
				1,520	Glass+CaO+rare C_3A	-----	-----
22	31.77	58.23	10	1,618	All glass	-----	-----
				1,615	(CaO liquidus)	-----	-----
				1,611	Glass+rare CaO	-----	-----
				1,500	Glass+CaO	-----	-----
				1,497	(C_3A appears as second phase)	-----	-----
				1,494	Glass+CaO+small amount of C_3A	-----	-----
23	27.44	52.56	20	1,520	All glass	1,383	-----
				1,517	(CaO liquidus)		
				1,515	Glass+rare CaO		
				1,472	Glass+CaO		
				1,470	(C_3A appears as second phase)		
				1,468	Glass+CaO+trace C_3A		
29	25.62	39.99	34.39	1,532	CaO+glass	-----	-----
25	21.57	40.43	38.00	1,398	All glass	1,388	-----
				1,397	(CaO liquidus)		
				1,396	Trace CaO+glass		
				1,395	CaO+C_3A+glass		

TABLE 1. *Quenching and DTA data for mixtures in the system* $CaO–CaO·Al_2O_3–2CaO·Fe_2O_3$—Continued

Mixture No.	Composition (Weight percent)			Quenching temperature	Phases present	Observed temperature of phase changes (DTA)	
	CaO	CA	C_2F			First liquid formation	Other phase changes
Mixtures having CaO as primary phase							
G64 [a]	21.20	38.80	40.00	1,380	Barely sintered, X-ray shows Fss + C_3A.	----	----
				1,384	do	----	----
				1,388	Little glass+much Fss+rare CaO +C_3A+growths.	----	----
				1,390	Little glass+Fss+little CaO+C_3A +growths.	----	----
				1,394	Mostly glass+rare CaO+little Fss +growths.	----	----
				1,400	Mostly glass+rare CaO, no Fss seen	----	----
48	23.18	28.32	48.50	1,473	All glass	1,387	1,399
				1,470	(CaO liquidus)		
				1,468	Glass+a little CaO		
32	21.13	28.99	49.88	1,455	All glass	1,389	1,402
				1,453	(CaO liquidus)		
				1,451	Glass+a little CaO		
49	19.59	18.11	62.3	1,530	Glass+trace of CaO+quench growths	1,415	----
				1,498	Glass+trace of CaO		
				1,480	Glass+small amount of CaO		
35	16.73	18.74	64.53	1,542	Glass+quench growth	1,416	----
				1,536	(CaO liquidus)		
				1,532	Glass+trace of CaO+quench growths.		
50	12.63	10.37	77	1,530	Glass+very rare CaO+quench growths.	1,425	----
				1,534	Glass+rare CaO+quench growths		
				1,520	Glass+CaO+quench growths		
51	4	----	96	1,449	Glass+quench growths	1,438	----
				1,440	Glass+CaO+quench growths		
Mixtures having Fss as primary phase							
58	17.77	62.23	20	1,370	All glass	----	----
				1,355	(Fss liquidus)	----	----
				1,351	Glass+rare Fss	----	----
				1,341	Glass+Fss	----	----
				1,340	($C_{12}A_7$ appears as second phase)	----	----
				1,339	Glass+Fss+trace of $C_{12}A_7$	----	----
78	12.46	62.01	25.53	1,359	All glass	----	----
				1,356	(Fs liquidus)	----	----
				1,352	Glass+Fss	----	----
71	8.0	58	34	1,379	All glass	----	----
				1,374	(Fss liquidus)	----	----
				1,370	Glass+a little Fss	----	----
7	18.34	51.66	30	1,384	All glass	1,334	1,367
				1,383	(Fss liquidus)		
				1,381	Glass+trace of Fss		
				1,377	Glass+moderate amount Fss		
75	16.2	50.0	33.8	1,400	All glass	----	----
				1,397	(Fss liquidus)	----	----
				1,395	Glass+small amount of Fss	----	----
				1,393	Glass+Fss	----	----
15	17.03	47.97	35	1,390	All glass	1,338	1,366
				1,389	(Fss liquidus)		
				1,386	Glass+Fss		
				1,370	Glass+Fss+C_3A		
76	15.8	48.3	35.9	1,411	All glass	----	----
				1,374	Glass+much Fss	----	----
36	18.45	43.84	37.71	----	----	1,385	----
39	17.24	44.49	38.27	1,400	All glass	1,385	----
				1,396	(Fss liquidus)		
				1,393	Glass+Fss+quench growths		
				1,391	(C_3A appears as second phase)		
				1,389	Glass+Fss+C_3A+quench growths		
C_4A_3F	16.02	45.15	38.83	1,398	All glass	1,367	1,389
				1,397	(Fss liquidus)		
				1,396	Glass+a little Fss		
				1,388	Glass+much Fss		
40	13.50	46.50	40	----	----	1,332	1,356
27	11.06	47.81	41.13	1,381	Glass+Fss+quench growths	1,342	1,382

[a] Made by M. A. Swayze.

TABLE 1. *Quenching and DTA data for mixtures in the system* CaO–$CaO \cdot Al_2O_3$–$2CaO \cdot Fe_2O_3$—Continued

Mixture No.	Composition (Weight percent)			Quenching temperature	Phases present	Observed temperature of phase changes (DTA)	
	CaO	CA	C_2F			First liquid formation	Other phase changes
Mixtures having Fss as primary phase							
6	15.72	44.28	40	1,403 1,397	All glass Glass+quench growths	1,371	1,386
26	21.18	38.82	40	1,394 1,393 1,386	All glass Glass+Fss+CaO+quench growths No glass, Fss+C_3A+quench growths	1,388	----
16	14.41	40.59	45	1,410	All glass	1,383	----
5	13.10	36.90	50	1,420 1,418 1,416	All glass (Fss liquidus) Glass+Fss	1,399	----
31	16.20	30.79	53.01	1,411 1,408 1,406 1,405	All glass Glass+quench growth (Fss liquids) Glass+rare Fss	1,390	1,401
37	14	31.61	54.39	----	----	1,388	1,399
C_4AF	11.54	32.52	55.94	1,426 1,424 1,422	All glass (Fss liquidus) Glass+trace of Fss	1,403	----
55	8.82	33.51	57.67	1,410 1,409 1,408 1,400	All glass (Fss liquidus) Glass+Fss+quench growths Glass+Fss+quench growths	1,338	1,399
30	6.35	34.41	59.24	1,410 1,361	Glass+quench growths Glass+some Fss+quench growths	1,323	1,366
4	10.48	29.52	60	1,434 1,421	Glass+quench growths Glass+Fss+quench growths	----	----
17	9.17	25.83	65	1,423 1,421 1,419	Glass+few quench growths (Fss liquidus) Glass+Fss+quench growths	1,412	1,422
3	7.86	22.14	70	----	----	1,428	1,433
34	11.73	19.87	68.40	1,425 1,416 1,414 1,412	Glass+quench growths Glass+Fss+quench growths (CaO appears as second phase) Glass+Fss+CaO+quench growths	1,416	----
38	9.89	20.28	69.83	1,418 1,417 1,416	Glass+Fss+quench growths CaO appears as second phase Glass+Fss+a little CaO+quench-growths.	1,415	1,423
41	8.65	20.57	70.78	----	----	1,418	----
C_4AF_2	7.40	20.85	71.75	----	----	1,427	----
42	4.57	21.48	73.95	----	----	1,420	----
33	1.74	22.12	76.14	----	----	1,206	1,409
18	6.55	18.45	75	----	----	1,421	1,428
59	6.04	15.96	78	1,421 1,400 1,391	Glass+Fss+quench growths Glass+Fss+quench growths Glass+Fss+small CaO crystals	1,423	----
77	7.0	11	82	1,430 1,422 1,421 1,420	Glass+very rare CaO Glass+Fss+quench growths (CaO appears as second phase) Glass+Fss+CaO+quench growths	---- ---- ---- ----	---- ---- ---- ----
19	3.92	11.07	85	----	----	1,426	1,430
1	2.62	7.38	90	1,464 1,457	Glass+quench growths Glass+quench growths	---- ----	---- ----
20	1.31	3.69	95	----	----	1,430	----
C_2F	----	----	100	----	----	1,439	----

Temperatures reported are accurate within ±5° C. Experience with repeated determinations of temperature for the same phase change indicates that the temperatures are reproducible within ±2° C. In order to conserve space, not all of the data are presented here but only those that suffice to establish the phase relations. The compositions of mixtures studied are shown in figure 2.

Primary phase regions occur for CaO, $3CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, $CaO \cdot Al_2O_3$, and calcium aluminoferrite solid solutions (Fss). The three calcium aluminates contain small amounts of CaO and Fe_2O_3 in

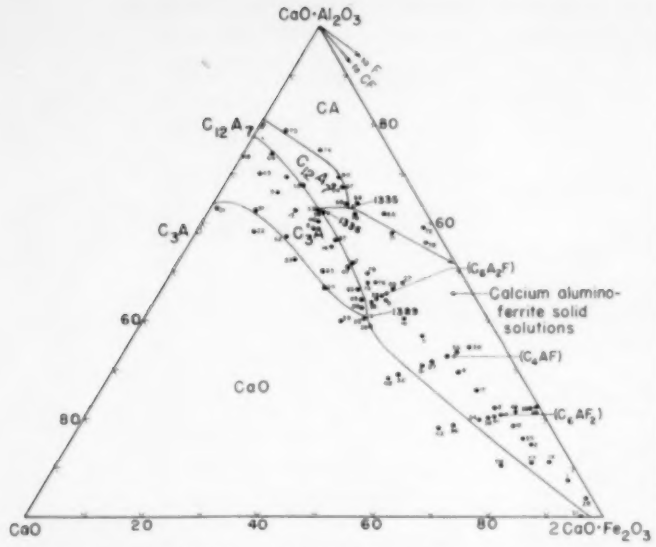

FIGURE 2. *Equilibrium diagram of the pseudo-ternary system* CaO-$CaO{\cdot}Al_2O_3$-$2CaO{\cdot}Fe_2O_3$ *showing compositions studied and primary phases.*

solid solution. The approximate limits of the calcium aluminate solid solutions, shown in figure 1, are taken from data reported by McMurdie [6] and by Yamauchi [7].

In general, phase boundaries and two of the invariant points determined are close to those reported by Swayze [8]. Some minor differences (table 2) exist in the compositions and temperatures of the invariant points at which (1) CaO, $3CaO{\cdot}Al_2O_3$, and a calcium aluminoferrite solid solution (Fss) and (2) $3CaO{\cdot}Al_2O_3$, $12CaO{\cdot}7Al_2O_3$, and Fss may occur in equilibrium with a liquid phase. To recheck differences between previously published data and the present work, a direct comparison has been made between mixture G64 synthesized by Swayze as the eutectic composition, and our No. 26 which has almost the same composition. The results are listed in table 1. In our study of Mix G64, all samples were held at temperature for 2 hr as described in the section headed Experimental Methods.

The composition determined in the present work for a third invariant point (E_3, fig. 1) at which $12CaO{\cdot}7Al_2O_3$, $CaO{\cdot}Al_2O_3$, and Fss can coexist with liquid is in reasonable agreement with that of McMurdie [6], although the temperature is approximately 10° higher than that reported by him.

The diagram presented in Swayze's report depicts a primary phase region for $6CaO{\cdot}2Al_2O_3{\cdot}Fe_2O_3$ distinct from the region of variable Fss composition. In the present work, however, the composition of the calcium aluminoferrite phase in equilibrium with liquid was found by X-ray powder diffraction measurements to change continuously with temperature over its primary phase region, and no second iron-bearing phase appeared. Along the E_2-E_3 boundary (fig. 1), however, the change in the Fss composition was so slight that it was not considered in constructing the diagram.

The compositions of the Fss phases in equilibrium at the invariant points and the assemblages of final crystallization products also differ from those reported by previous investigators [2, 6, 8]. These results will be discussed in greater detail in the sections that follow.

3.2. Calcium Aluminoferrite Solid Solutions

In figures 1[5] and 3, a single-phase region of calcium aluminoferrite solid solutions is designated by the shaded area extending from $2CaO{\cdot}Fe_2O_3$ toward the CaO-$CaO{\cdot}Al_2O_3$ boundary of the system.

X-ray powder diffraction patterns of devitrified glasses with compositions along the line X-Y (fig. 3) confirmed $3CaO{\cdot}Al_2O_3$ and Fss to be the final products of crystallization for $6CaO{\cdot}2Al_2O_3{\cdot}Fe_2O_3$ and neighboring glasses with higher CaO content. These compositions are, therefore, not in the single-phase (solid solution) region, but are on the high-CaO side of it. Mixtures No. 40 and 27, on the other hand, each showed $CaO{\cdot}Al_2O_3$ and Fss as devitrification products and are on the low-CaO side of the Fss band.

In figure 4 the ratios of intensities of selected diffraction peaks for $3CaO{\cdot}Al_2O_3$ or $CaO{\cdot}Al_2O_3$ to those of a peak of the tungsten internal standard in the same pattern have been plotted against the

[5] For reasons of limited space, compounds and phases are referred to by symbols. For example: C=CaO; A=Al_2O_3; F=Fe_2O_3; and Fss=calcium-aluminoferrite solid solution. Thus, $C_4AF=4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$.

TABLE 2. *Invariant points for the pseudoternary system* CaO–$CaO{\cdot}Al_2O_3$–$2CaO{\cdot}Fe_2O_3$n

Phases	Authority	Composition percentage						Temperature, ±5° C
		CaO	Al_2O_3	Fe_2O_3	CaO	$CaO{\cdot}Al_2O_3$	$2CaO{\cdot}Fe_2O_3$	
								°C
CaO–C_3A–Fss (or C_4AF)	W. C. Hansen, L. T. Brownmiller, and R. H. Bogue.	54	37	9	.....	.....	.....	1,340
	H. F. McMurdie	53	32	15	.....	.....	.....	1,370
	M. A. Swayze	51.4	25.0	23.6	.....	.....	.....	1,380
	Present investigation	51.1	26.5	22.4	20.8	41.0	38.2	1,380
C_3A–$C_{12}A_7$ (or C_3A_3)–Fss (also C_4AF or C_6A_2F).	W. C. Hansen, L. T. Brownmiller, and R. H. Bogue.	47	43	10	.....	.....	.....	1,335
	H. F. McMurdie	48	38	14	.....	.....	.....	1,335
	M. A. Swayze	48.5	40.5	11.0	.....	.....	.....	1,335
	Present investigation	48.4	40.3	11.3	18.3	62.4	19.3	1,336
$C_{12}A_7$ (or C_3A_3)–CA–Fss (or C_4AF).	W. C. Hansen, L. T. Brownmiller, and R. H. Bogue.	42	40	18	.....	.....	.....	1,320
	H. F. McMurdie	45	40	15	.....	.....	.....	1,315
	Present investigation	45.1	40.6	14.2	12.8	63.0	24.2	1,335

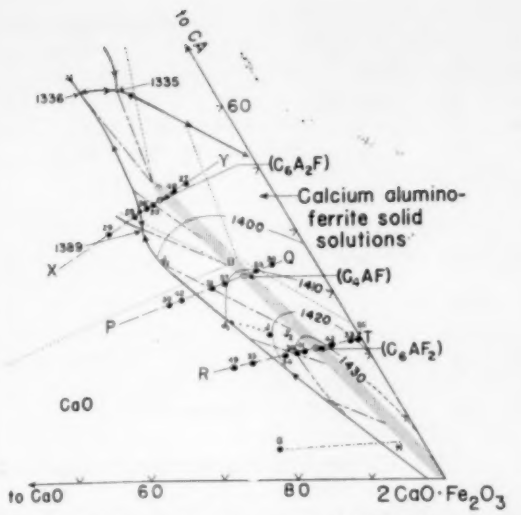

FIGURE 3. *Calcium aluminoferrite solid-solution regions in the pseudo-ternary system* CaO-$CaO \cdot Al_2O_3$-$2CaO \cdot Fe_2O_3$ *with tie lines and typical crystallization paths.*

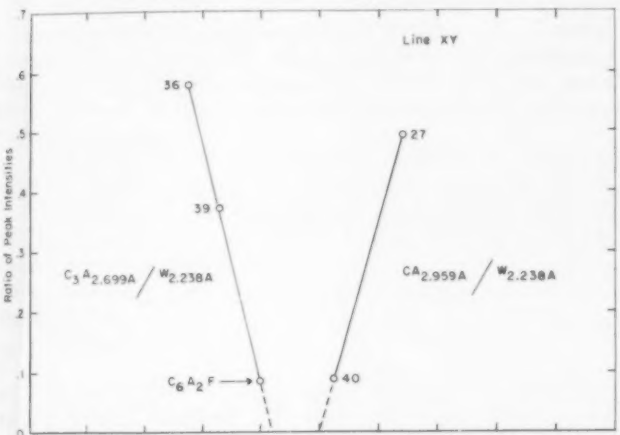

FIGURE 4. *Relationship between the CaO content and the relative intensities of selected* $3CaO \cdot Al_2O_3$ *and* $CaO \cdot Al_2O_3$ *peaks as compared with standard tungsten peaks in X-ray powder diffraction patterns of devitrified glasses with compositions along the line XY (see fig. 3).*

percentage of the CaO component for these devitrified glasses. The approximate width (2% CaO) of the solid-solution band in this region has been determined by extrapolating the two curves obtained by the above procedure to a zero ratio. A similar treatment (fig. 5) gives the approximate width of the Fss band along line P–Q (fig. 3) at $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

For compositions on the line R–T in figure 3, the secondary phase on the low CaO side of $6CaO \cdot Al_2O_3 \cdot 2Fe_2O_3$ is $CaO \cdot Fe_2O_3$ (with a small amount of $CaO \cdot Al_2O_3$ in solid solution). Most of the principal diffraction maxima for the latter compound correspond closely to those for some members of the calcium-aluminoferrite solid-solution series. Because of this interference the low CaO limit of the Fss band could not be determined as closely in this region by the X-ray diffraction method. It was observed (table 1), however, that the differential

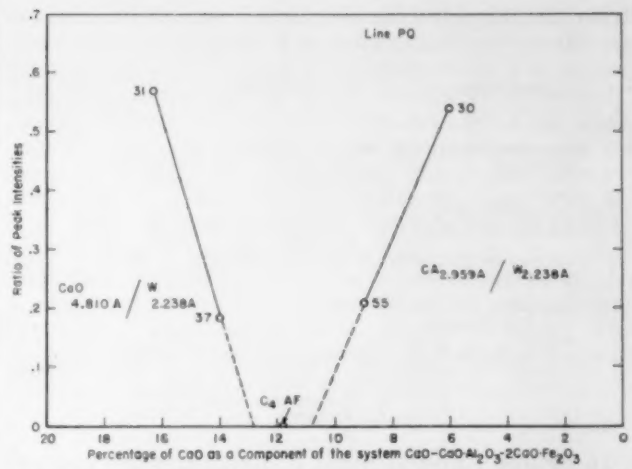

FIGURE 5. *Relationship between the CaO content and the relative intensities of selected* CaO *and* $CaO \cdot Al_2O_3$ *peaks as compared with standard tungsten peaks in X-ray powder diffraction patterns of devitrified glasses with compositions along the line PQ (see fig. 3).*

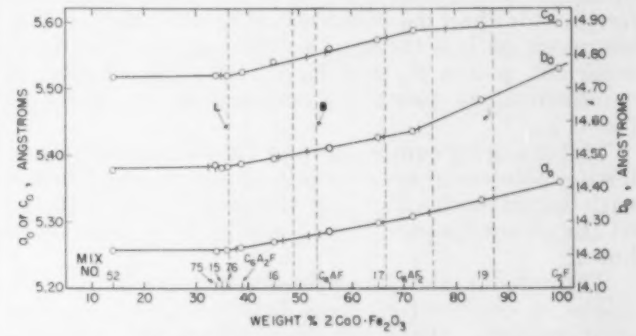

FIGURE 6. *Selected interplanar spacings* (d_{hkl}) *characteristic of the iron-bearing solid-solution phase for mixtures along the line* C_2F-*L (fig. 1).*

Dotted lines show compositions of Fss phase at ends of tie lines.

temperature curves in DTA patterns of mixtures with compositions found by the X-ray method to be near but outside of the solid-solution band contained two peaks, whereas curves of mixtures within the band contained only one. This characteristic made it possible to define more closely than by the X-ray method the limit of solid solution in the $6CaO \cdot Al_2O_3 \cdot 2Fe_2O_3$ region in the direction away from the CaO vertex.

Unit-cell dimensions for the Fss phase in completely crystallized mixtures with compositions in or near the single-phase (solid-solution) band are plotted as a function of composition in figure 6. These dimensions are based on interplanar spacings obtained from X-ray powder diffraction patterns by the authors, together with indices reported by Malquori and Cirilli [10]. A change in the slopes of the curves for a_0, b_0, and c_0 in figure 6 occurs near the composition $6CaO \cdot Al_2O_3 \cdot 2Fe_2O_3$, which may represent an ordering of the structure. Lattice parameters continue to change with further compositional changes to point L, however, and the region is, therefore, shown on the phase diagram as one of continuous solid solution.

TABLE 3. *Significant calcium aluminoferrite solid-solution compositions for the pseudoternary system CaO-CaO·Al_2O_3-2CaO·Fe_2O_3*

Designation	Authority	Composition percentage						Molecular formula
		CaO	Al_2O_3	Fe_2O_3	CaO	CaO·Al_2O_3	2CaO·Fe_2O_3	
1. Solid solution limit (high-Al_2O_3 end).	W. C. Hansen, L. T. Brownmiller, and R. H. Bogue.	46.1	21.0	32.9	11.4	32.6	56.0	$4CaO·Al_2O_3·Fe_2O_3$
C_6A_2F	M. A. Swayze	48.07	29.12	22.81	16.0	45.1	38.8	$6CaO·2Al_2O_3·Fe_2O_3$
Solid solution limit	T. Yamauchi	-------	-------	-------	-------	-------	-------	$6.2CaO·2.2Al_2O_3·Fe_2O_3$
Solid solution limit	G. L. Malquori and C. L. Cirilli.	-------	-------	20.5	-------	-------	34.9 by weight.	
Solid solution limit Point L (fig. 1).	Present investigation	47.78	31.13	21.09	15.7	48.0	36.3	$6.37CaO·2.28Al_2O_3·Fe_2O_3$
2. Composition at CaO-C_3A-Fss invariant point:								
Point B (fig. 1)	Present investigation	45.95	23.06	30.99	11.50	35.75	52.75	$4.3CaO·1.1Al_2O_3·Fe_2O_3$
Point VIII	M. A. Swayze	45.57	18.01	36.42	10.07	27.92	62.00	
C_4AF	W. C. Hansen, L. T. Brownmiller, and R. H. Bogue.	46.1	21.0	32.9	11.4	32.6	56.0	$4CaO·Al_2O_3·Fe_2O_3$

In figures 1 and 7, point L designates the limit of solid solution, determined in the present investigation, in the direction of the CaO-CaO·Al_2O_3 boundary. The composition represented by point L agrees well with those reported by Yamauchi [7] and by Malquori and Cirilli (see table 3). It contains less ferric oxide than the composition $6CaO·2Al_2O_3·Fe_2O_3$. Composition L is the solid solution in equilibrium at invariant points E_2 and E_3. The solid solution in equilibrium at point E_1 corresponds to point B (table 3).

The changing composition of the calcium-aluminoferrite solid-solution crystals (Fss) in equilibrium with liquid with changing temperature is depicted on the phase diagram (figs. 1 and 3) by a series of tie lines.

Throughout the Fss primary region, large variations in composition have little effect on liquidus temperatures. This behavior causes the composition of the liquid formed in a mixture in this region to reach a primary-phase boundary only a few degrees below the liquidus temperature. The tie lines of importance, therefore, are those that indicate the compositions of the Fss phase in equilibriun with liquids on the phase boundaries and at invariant points that bound the Fss region. Seven such tie lines have been established in this investigation.

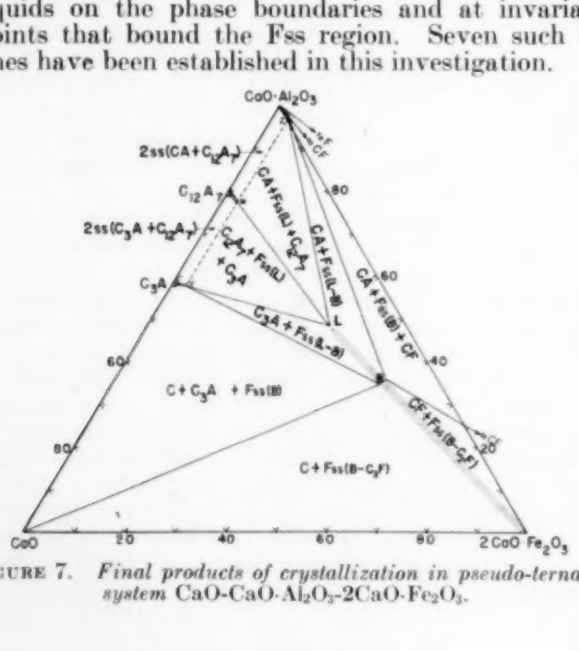

FIGURE 7. *Final products of crystallization in pseudo-ternary system* CaO-CaO·Al_2O_3-2CaO·Fe_2O_3.

3.3. Crystallization in the System

In the pseudoternary system CaO-CaO·Al_2O_3-2CaO·Fe_2O_3 there are 11 areas in which compositions may fall with regard to their final products of equilibrium crystallization. These are designated in figure 7. In only 4 of these regions is crystallization completed (or melting begun) at an invariant point. These are the composition triangles [6] with their respective invariant temperatures:

(1) CaO-3CaO·Al_2O_3-Fss(B) 1,389° C.
(2) 3CaO·Al_2O_3-12CaO·7Al_2O_3-Fss(L) 1,336° C.
(3) 12CaO·7Al_2O_3-CaO·Al_2O_3-Fss(L) 1,335° C.
(4) CaO·Al_2O_3-Fss(B)-CaO·Fe_2O_3 (Invariant point outside pseudosystem limits.)

Mixtures with compositions in any one of the above four triangles will, on heating under equilibrium conditions, begin to melt at the temperature indicated. The composition of the first liquid formed will be that of the invariant point (table 2 and fig. 1) at which the three designated crystalline phases can exist in equilibrium with liquid. Conversely, on cooling these mixtures, the last bit of liquid will have the composition of the invariant point and will disappear at the invariant temperature. The specimen will then consist of the three crystalline phases at the vertices of the triangle.

Compositions in 6 of the areas complete their crystallization on a phase boundary. These two-phase areas are designated in figure 7 by their final products of equilibrium crystallization, viz:

(1) CaO·Al_2O_3 + Fss(L-B)
(2) 3CaO·Al_2O_3 + Fss(L-B)
(3) CaO + Fss(B-C_2F)
(4) CaO·Fe_2O_3 + Fss(B-C_2F)
(5) 2 solid solutions (3CaO·Al_2O_3 + 12CaO·7Al_2O_3)
(6) 2 solid solutions (12CaO·7Al_2O_3 + CaO·Al_2O_3).

[6] As indicated in figures 1 and 7, all of the compounds listed, except CaO, contain some material in solid solution. The variations in composition are small, however, and of little importance in comparison with the range of calcium aluminoferrite solid solutions (Fss). For convenience the symbol "ss", indicating a solid solution, is used in the text only to designate the calcium aluminoferrite series, or single compositions in this series.

In each of the six areas, the temperature at which a liquid is first formed on heating, or disappears on cooling, varies with composition. At least one of the products of crystallization, however, will consist of a solid solution whose composition will also vary with the composition of the mixture.

Thus for the triangle labeled "C+Fss(B-C_2F)" (fig. 7), the products at complete equilibrium crystallization will consist of CaO and a calcium aluminoferrite solid solution whose composition is between point B and C_2F.

For a given mixture in one of the six 2-phase areas, the final composition of the Fss phase is determined by a line from the composition of the other crystallization product through the composition of the mixture, and extended to the boundary of the *single-phase* Fss area (largest shaded area). The point at which the line intersects this boundary is the composition of the Fss crystallization product. An example in figure 3 is composition G; a line from the CaO vertex through G intersects the boundary of the shaded area at H, the composition of the Fss phase in mixture G when crystallization is completed.

In the 11th area, the shaded Fss area, all compositions after crystallization consist of one phase, a calcium aluminoferrite solid solution having the same composition as the original mixture.

In addition to the 11 areas discussed above, shading near $3CaO{\cdot}Al_2O_3$ and $12CaO{\cdot}7Al_2O_3$ in figures 1, 7, and 8 indicates solid solutions along the lines $3CaO{\cdot}Al_2O_3$-V and $12CaO{\cdot}7Al_2O_3$-W respectively. There is also a small shaded area near $CaO{\cdot}Al_2O_3$ representing a ternary solid solution just beyond the pseudosystem boundary. The product of crystallization of compositions in each of these regions is also a single solid solution.

Compositions in the shaded portions of the diagram complete their crystallization at temperatures for corresponding points on the solid-solution solidus. These points are below the projected liquidus surface in figure 1, and for those regions the solidus temperatures cannot be determined from the figure. All mixtures studied do have Fss as an equilibrium product of crystallization and the first liquid formation temperature is the solidus temperature for the Fss phase that is present. The temperatures of first liquid formation are given for most of the mixtures in table 1, and for mixtures in the Fss primary phase region these solidus temperatures can be compared directly with the corresponding Fss liquidus temperatures.

The pseudosystem CaO-$CaO{\cdot}Al_2O_3$-$2CaO{\cdot}Fe_2O_3$ is unusual inasmuch as it contains examples of most of the major types of equilibrium crystallization. Furthermore, the system contains an extensive series of ternary solid solutions with intermediate and end members (B and L, respectively, fig. 1) that exhibit some of the characteristics of incongruently melting compounds. These complicate the crystallization process.

It should be noted in figures 1, 3, and 8 that the liquidus maximum on the phase boundary separating the $3CaO{\cdot}Al_2O_3$, and the Fss primary phase regions occurs not at the intersection of the boundary with the line V-B, but at a nearby point where the tie lines from V and from the single-phase Fss region (the large, shaded area) become collinear. Similarly, the maximum on the boundary between $CaO{\cdot}Al_2O_3$ and Fss regions occurs at the point where the tie lines to Z and the single-phase Fss region become collinear. A similar configuration was reported by Roy and Osborn [14] for the system $Li_2O{\cdot}SiO_2$-$Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$-$SiO_2$.

Almost any composition to be encountered in the ternary system can be classified under one of four types of crystallization to be discussed here. The exceptions are compositions in the shaded regions

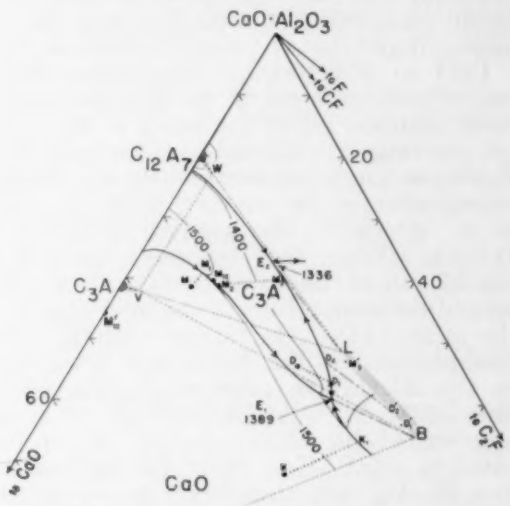

FIGURE 8. *A portion of the equilibrium diagram showing paths of crystallization followed by typical mixtures within the system.*

C_3A and $C_{12}A_7$ solid solutions are treated as having the constant composition V and W.

(figs. 1 and 7) for which, as mentioned previously, only approximate liquidus temperatures and final crystallization products can be determined from the ternary diagrams.

For convenience, the equilibrium crystallization of compositions in the system will be discussed in terms of cooling chosen mixtures from a temperature at which they are completely melted to a temperature at which all liquid disappears. It will be assumed that equilibrium exists in all phases throughout the process, although this situation may be difficult to approximate in actual practice.

As the first example, consider the composition (fig. 8) represented by point K in the triangle CaO-C_3A-B. On cooling this mixture, crystals of CaO appear at the liquidus temperature. With continued cooling, CaO continues to crystallize and the composition of the liquid moves along the line K-K_1 until it reaches the point K_1 on the CaO-Fss phase boundary. With further cooling, the composition of the liquid follows the CaO-Fss phase boundary from K_1 to the eutectic at E_1. Both Fss and CaO are in equilibrium with liquid in this temperature range. After the liquid composition has reached E_1 (at the

eutectic temperature, 1,389° C), crystals of $3CaO \cdot Al_2O_3$ appear. At the minimum heat content, the charge will be completely crystallized and will consist only of CaO, Fss(B), and $3CaO \cdot Al_2O_3$.

The crystallization of a composition M (Mix No. 22, table 1) in the triangle V-W-L follows a somewhat more complex pattern. On cooling M from its liquidus temperature of 1,615° C, CaO crystallizes as the primary phase and the liquid composition moves directly away from the CaO vertex along a line $M\text{-}M_1$. At M_1, $3CaO \cdot Al_2O_3$ appears as a secondary crystalline phase. With further cooling, the liquid composition then moves down the boundary between the CaO and $3CaO \cdot Al_2O_3$ regions until it reaches point M_2. In the temperature range in which the liquid composition is changing from M_1 to M_2, the mean composition of the solid phases is changing from CaO to $3CaO \cdot Al_2O_3$. Neglecting the small amount of solid solution in the calcium aluminate, the mean composition of the solids at any temperature in this range is obtained by drawing a line from the corresponding liquid composition M_{12} through M (the composition of the mixture) to the point M'_{12} at which it intersects the system boundary $CaO\text{-}3CaO \cdot Al_2O_3$. When the composition of the liquid reaches M_2, all of the crystalline CaO will have dissolved and the composition of the solid phase present will be $3CaO \cdot Al_2O_3$. On further cooling, therefore, the composition of the liquid will move directly across the $3CaO \cdot Al_2O_3$ primary phase region along the line $M\text{-}M_2\text{-}M_3$. At M_3 crystals of a calcium aluminoferrite solid solution having the composition indicated by point M'_3 at the end of the interpolated tie line, $M_3\text{-}M'_3$, will then begin to crystallize. As the temperature is lowered, the composition of the liquid will move along the $3CaO \cdot Al_2O_3$-Fss phase boundary to E_2 at 1,336° C at which point crystallization will be completed. Mixture M will then be composed of crystals of $3CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, and Fss (L).

During crystallization, the changing liquid compositions for mixtures in the Fss primary phase region may be represented on the phase diagram by curved lines. The curvature results from the fact that in this region the composition of the solid (Fss) phase is also changing with temperature.

In figure 3, a portion of the approximate crystallization path for mixture J in the Fss primary-phase region and the composition triangle $CaO\text{-}B\text{-}C_2F$ is designated by the dotted line $J\text{-}J_1$. This path is typical of those for other mixtures in the same region. Additional crystallization paths in the same area are not shown inasmuch as compositions in this area form liquids having compositions on the CaO-Fss phase boundaries at only a few degrees below the respective liquidus temperatures of the mixtures.

The composition J_1 is defined by that member of the indicated family of the tie lines which passes through J. After reaching J_1, the composition of the liquid on further cooling will follow the CaO-Fss phase boundary in the direction of decreasing temperature until the solid solution, as defined by the family of tie lines, reaches a composition J'_2 on the straight line defined by J and the CaO vertex. The liquid composition at the conclusion of crystallization is the end of the tie line from J'_2, or the point J_2. The final products of equilibrium crystallization for mixture J will thus be CaO and an Fss phase having the composition J'_2.

Other tie lines in the phase diagram designate compositions of the Fss phase found to coexist with designated liquid compositions along the phase boundaries. For intermediate points (such as D_1, fig. 8), the approximate compositions of the coexisting liquid and solid phases can be determined by graphical interpolation of the given tie lines. For each mixture in a two-phase area, the point which represents the composition of the liquid when crystallization is completed will be on the phase boundary at the end of the tie line that connects with the composition of the final Fss crystallization product for the mixture.

Mixture D (fig. 8) represents another typical composition in a two-phase area. Here $3CaO \cdot Al_2O_3$ is the primary phase and it continues to crystallize as the temperature is lowered until the liquid reaches the phase boundary at D_1. At this point, an infinitesimal amount of Fss having approximately the composition D'_1 (on an interpolated tie line, $D_1\text{-}D'_1$) begins to crystallize. The liquid composition then moves along the C_3A-Fss boundary until the solid solution composition reaches a point D'_2 defined by the straight line through V and D. At the completion of crystallization, the liquid composition is D_2, the end of the tie line from D'_2. Mixture D is then composed of $3CaO \cdot Al_2O_3$, and Fss of composition D'_2.

4. Application to Portland Cement Chemistry

The extent to which information on the ternary system can be applied directly to the manufacture of portland cement clinker containing many components is, of course, limited. Nevertheless, because of similarity of the phases actually observed in commercial clinkers to some of those appearing in simpler systems, useful extrapolations of phase relations in these systems can help to explain the behavior of the more complex compositions.

It is generally conceded, as a result of previous investigations [2, 7, 8, 9], that the principal iron-bearing phase in portland cement clinker is essentially a calcium aluminoferrite of variable composition. In commercial clinkers it is likely that this phase contains also small amounts of additional components in solid solution. As a first approximation, however, its composition can be considered as falling within the limits of the shaded single-phase Fss area on the phase diagram in figure 1.

It is evident from figures 1 and 7 that even the composition of the final Fss phase, formed by complete equilibrium crystallization, can vary widely with different mixtures in the system. This variability results from the fact that there are wide ranges of composition (the six 2-phase areas) for which crystallization is completed on a phase boundary, rather than at an invariant point. The variability applies to the temperature at which

liquid is first formed or disappears in the different mixtures as well as to the composition of the Fss phase.

Only in the single-phase Fss region and the two-phase CaO-Fss region will the Al_2O_3/Fe_2O_3 ratio of the Fss phase always be the same as that of the original mixture.

The one- and two-phase areas in the ternary system (fig. 7) may be expected to bound analogous regions in multicomponent clinker systems in which both the final composition of the Fss phase and the solidus temperature will vary with the composition of the mixture. *Even if equilibrium were attained*, therefore, for commercial portland clinkers the temperature at which liquid is first formed during burning, the quantity of liquid produced in the hot zone of the kiln, and the constitution of the clinker can differ considerably for cement raw mixtures of different Al_2O_3/Fe_2O_3 ratios. The Al_2O_3/Fe_2O_3 weight ratio in the iron-bearing phase can presumably vary with different mixtures from 0 to 1.476, with accompanying effects on the percentages of the other clinker constituents.

Although the presence of Fe_2O_3 in the mix causes the formation of a liquid phase at a lower temperature than if it were absent, increasing the percentage of Fe_2O_3 in the raw mix does not necessarily cause easier burning, but may even have the opposite effect. Study of figure 1 reveals that mixtures whose crystallization is completed along the CaO-Fss phase boundary, or at E_1 (eutectic temperature, 1,389° C) will be more difficult to burn than mixtures completing their crystallization at invariant points E_2 and E_3.

Optimum conditions for proportioning and burning given raw materials of known chemical compositions to produce clinker of the desired constitution and burning characteristics cannot be determined from the phase diagram for the ternary system alone. Additional work is still required on portions of the quaternary system $CaO\text{-}Al_2O_3\text{-}Fe_2O_3\text{-}SiO_2$. Specifically needed in the four-component system are additional tie lines showing the compositions of the Fss phase in equilibrium with liquids along phase boundaries, and a further subdivision of the system into composition spaces that define the final products of crystallization within each region. Such a subdivision provides information on the quaternary system analogous to that given in figure 7 for the ternary system.

The authors are indebted to M. A. Swayze for his generous cooperation in making available to them for reference, his slides, mixtures, and notes on the ternary system $CaO\text{-}5CaO\cdot3Al_2O_3\text{-}2CaO\cdot Fe_2O_3$. They also express thanks to A. C. Bonanno and R. L. Wadlinger for their help in obtaining X-ray and quenching data presented in this paper.

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Heats of Formation of Diborane and Pentaborane

Edward J. Prosen, Walter H. Johnson, and Florence Y. Pergiel

The heats of formation of diborane and pentaborane have been determined by measurements of the heats of decomposition into amorphous boron and hydrogen in a calorimeter. The heats of formation at 25° C, from amorphous boron and hydrogen, are 6.73 ±0.52 kcal/mole for diborane (gas) and 12.99 ±0.39 for pentaborane (gas).

1. Introduction

In order to ascertain the bond energy relations in the boron hydrides, precise values of the heats of formation of these substances from the elements are needed. Diborane, B_2H_6, and pentaborane, B_5H_9, were chosen for investigation as two of the simplest members of this class of compounds.

The measurements reported in this paper were made in 1948 but have not been previously published. No value for the heat of formation of pentaborane was available at that time. The value for the heat of formation of diborane given by Roth and Börger, −44 kcal/mole, [1, 2][1] was based on measurements of the heat of hydrolysis of diborane to boric acid, the heat of combustion of boron to boric oxide, and the heat of solution of boric oxide. This value was very uncertain because it depended directly upon the heat of combustion of elemental boron, a quantity which could not be determined with any precision. However, it was found that diborane and pentaborane could be decomposed quantitatively and rapidly at 600° C into amorphous boron and gaseous hydrogen. Hence this decomposition reaction could be employed calorimetrically to give values of the heats of formation of diborane and pentaborane independent of the value for the heat of combustion of boron.

2. Experimental Procedure

2.1. Materials

The diborane and pentaborane samples were obtained from the Naval Research Laboratory, Washington, D. C., through the courtesy of R. R. Miller. A similar sample of diborane supplied to the Ohio State University was found by the cryoscopic method to have a purity of 99.95 mole percent [3].

The pentaborane was produced by the fractional pyrolysis of diborane. A sample of the same lot supplied to the Ohio State University was found by the cryoscopic method to have a purity of 99.97 mole percent [4]. Analysis by the mass spectrometer showed no impurities other than boron hydrides with none heavier than B_5H_9 [5].

2.2. Apparatus

The calorimeter was of the isothermal-jacket type; the jacket temperature was maintained constant within ±0.001° C during each experiment. Details of the calorimeter assembly have been described in previous reports from this laboratory [6,7].

[1] Figures in brackets indicate the literature references at the end of this paper.

The calorimetric vessel used for the decomposition of diborane and pentaborane is shown in figure 1. It consisted essentially of a quartz tube (A) upon which was wound a nichrome wire heating coil (B) surrounded by a silver radiation shield (C) and a vacuum jacket (D). The heating coil had a total resistance of 190 ohms and was tapped (E) so that the upper portion had a resistance of 127 ohms. Quartz wool plugs (F) were inserted in the tube above and below the heating coil to retain the solid products within the heated zone. The exit vapors were carried out through the glass helix (G) to cool them to the calorimeter temperature.

Calorimeter temperatures were determined by means of a platinum resistance thermometer in conjunction with a Mueller bridge. The quantity of electrical energy was determined from the current, voltage, and time of current flow. The current and voltage were determined by means of a White double

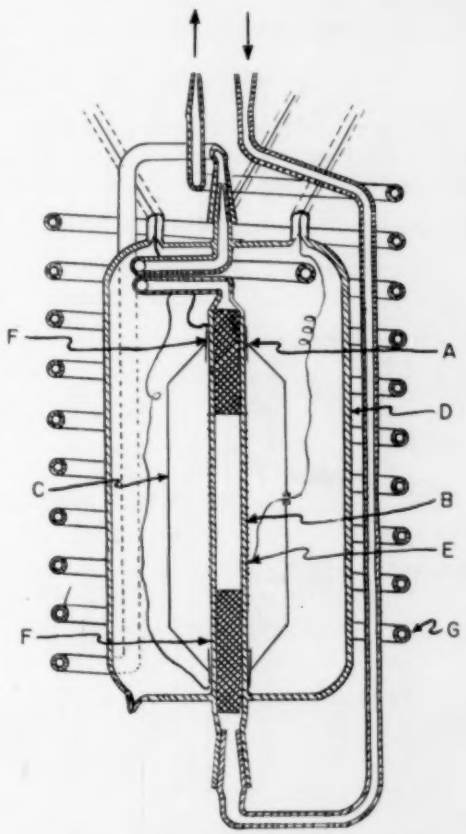

FIGURE 1. *Calorimetric reaction vessel.*

potentiometer from measurements of the potential drop across appropriate standard resistors included in the power circuit [8]. Timing of the experiments was done by reference to standard seconds-signals produced at the National Bureau of Standards. All equipment was calibrated in terms of standards maintained at the Bureau.

2.3. Procedure

a. Reaction Experiments

(1) *Diborane.* The gas train used for the diborane decomposition experiments is shown in figure 2. The diborane was contained in a steel cylinder fitted with a needle valve and connected to the system through a flowmeter and a mercury float valve. Before each experiment the cylinder was immersed in liquid nitrogen, and traces of hydrogen (produced by slow decomposition of diborane into higher boranes) were removed by evacuation. After removal of the hydrogen the valve was closed and dry ice was substituted for the liquid nitrogen; at the temperature of dry ice, the vapor pressure of diborane is approximately 2 atm and the vapor pressures of the higher boranes are negligible. Helium was passed through the system at a constant rate throughout the experiment. It was purified by passing successively over copper oxide at 600° C, ascarite, magnesium perchlorate, and phosphorus pentoxide before it entered the system.

Temperatures were observed at 2-min intervals during a 20-min "fore" rating period. At the end of this period the current was switched from an external "spill" resistor (having the same resistance as the heater) into the upper portion of the calorimetric vessel. After a warm-up period of 2 min the needle valve was opened, which permitted the diborane to pass into the vessel. The flow of diborane was cut off after 16 min and the float valve closed. Four minutes later the current was switched to pass through both portions of the heater; this completed the decomposition of the polymerized material usually formed near the lower end of the upper portion of the heater. By means of appropriate resistors in the circuit, the current was nearly constant in both cases. During this time readings of current and voltage were made on alternate minutes, and temperature readings were made at 1-min intervals. When the desired calorimeter temperature was obtained the electric current was discontinued. Temperature measurements were continued at 1-min intervals until thermal equilibrium was reestablished, after which observations were made at 2-min intervals during a 20-min "after" rating period.

The gas mixture of helium and hydrogen passed out of the calorimeter through a trap cooled in liquid nitrogen, a copper oxide furnace maintained at 600° C, and a weighed absorption tube containing magnesium perchlorate and phosphorus pentoxide.

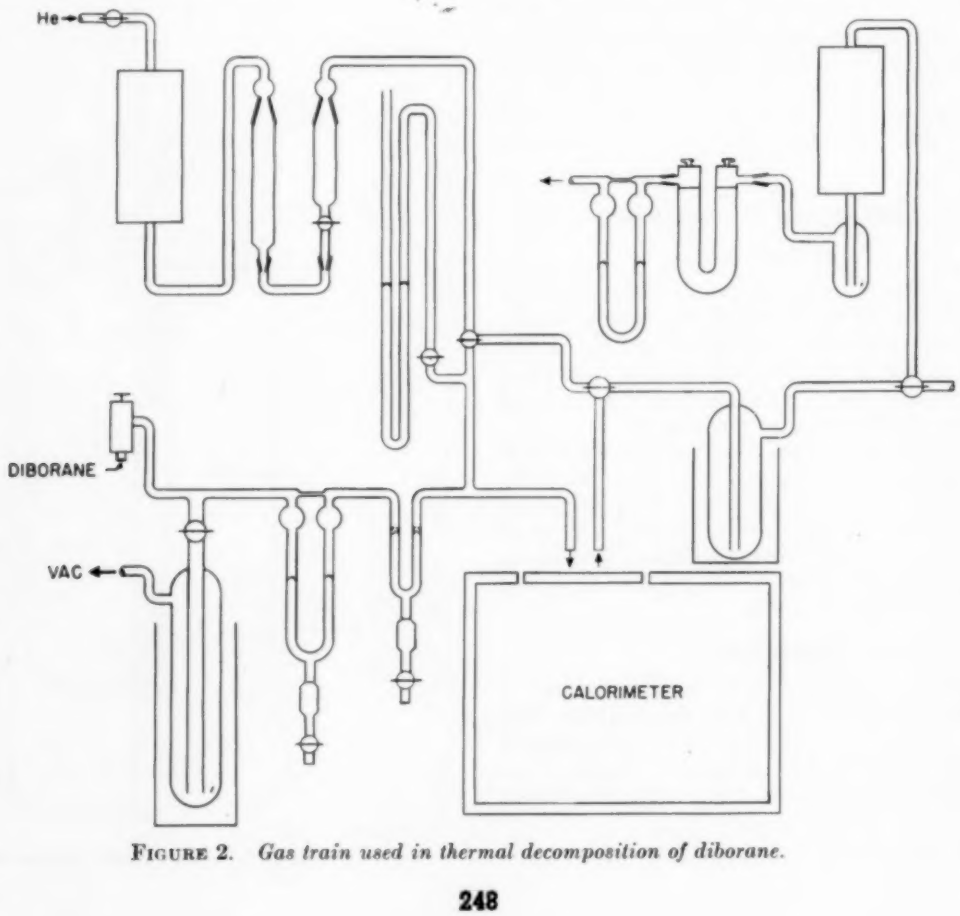

FIGURE 2. *Gas train used in thermal decomposition of diborane.*

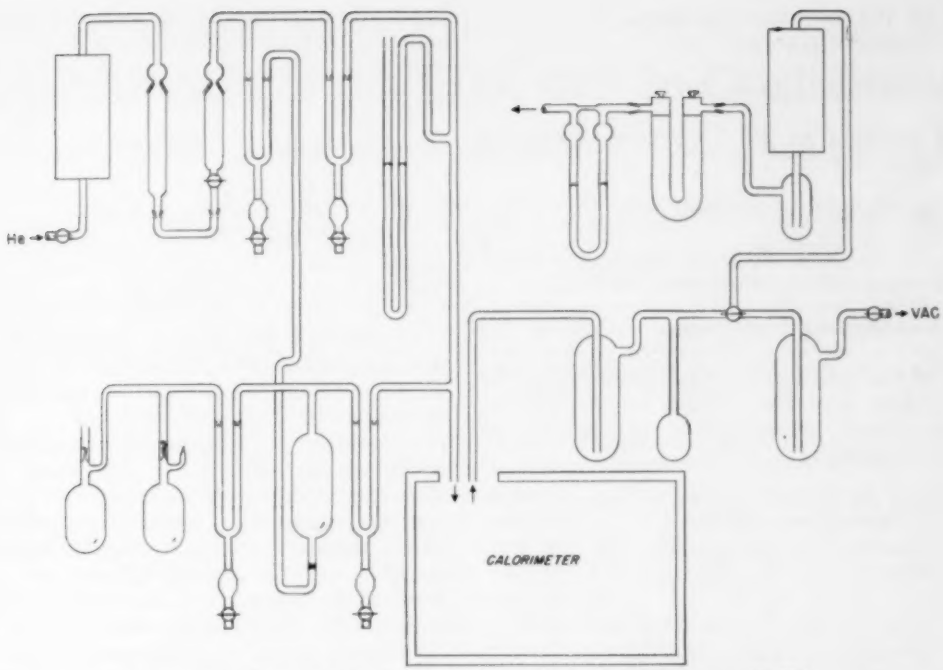

FIGURE 3. *Gas train for use in decomposition of pentaborane* (B_5H_9).

The trap was included as a safety measure, to prevent the diborane from reaching the furnace in the event of incomplete decomposition. No material was collected in the trap in any of these experiments.

The quantity of reaction was determined from the amount of hydrogen which was burned in the furnace and collected in the absorption tube as water.

(2) *Pentaborane.* The gas train used in the experiments with pentaborane is shown in figure 3. The pentaborane was inclosed in an internal breakoff ampoule. For each experiment the system was evacuated and a portion of the pentaborane transferred into the bubbling vessel. The experiments were carried out in the same manner as with diborane except that purified helium was bubbled through the pentaborane at 0° C in order to carry it into the calorimetric vessel. After each experiment, the remainder of the pentaborane in the bubbler, as well as that remaining in the original ampoule, was transferred to a second ampoule and sealed in vacuum.

b. Calibration Experiments

The calibration experiments were performed in exactly the same manner and using the same system as with the decomposition experiments except for omission of the boron hydride. Because the system used for pentaborane differed slightly from that used for diborane, a separate series of calibration experiments was performed.

3. Results

The results of the calibration experiments for the diborane system are given in table 1 in which E corresponds to the electrical energy added to the system, ΔRc the increase in resistance of the platinum thermometer, and $E_s = E/\Delta Rc$, the energy equivalent of the system.

The results of the diborane decomposition experiments are given in table 2, where q is the total energy absorbed by the system and is given by the following relationship:

$$(\Delta Rc)(E_s) = q.$$

This value of q when corrected for q_g, the correction calculated from the heat capacities of the gases involved, and subtracted from E, the electrical

TABLE 1.—*Results of the electrical calibration experiments on the diborane system*

Experiment	E	ΔR_c	E_s
	j	*Ohm*	*j/ohm*
1	49480.9	0.381239	129790
2	50329.8	.387803	129782
3	49804.4	.383708	129798
4	51630.9	.397799	129791
5	49551.6	.381761	129797
Mean			129792
Standard deviation of the mean			±3

TABLE 2. *Results of the diborane decomposition experiments*

Experiment	E	ΔR_c	q	q_g	q_s	B_2H_6	$-\Delta H$ (25° C)
	j	*Ohm*	*j*	*j*	*j*	*Mole*	*kj/mole*
1	51311.2	0.397528	51596.0	0.6	−284.2	0.010206	27.85
2	48536.9	.379034	49195.6	−2.2	−660.9	.021851	30.25
3	48557.9	.377216	48959.6	2.3	−399.4	.015966	25.02
4	49008.7	.379105	49204.8	1.1	−195.0	.007213	27.04
5	48704.1	.376538	48871.6	0.3	−167.2	.005444	30.71
Mean							28.17
Standard deviation of the mean							±1.05

energy added to the system, yields q_c, the energy absorbed by m moles of reaction, or:

$$E-(q-q_s)=q_c.$$

The heat of reaction at 25° C is then given by the ratio of q_c to m, or:

$$q_c/m=\Delta H \text{ joules/mole.}$$

To convert to the conventional thermochemical calorie, the following relationship was used:

$$1 \text{ calorie}=4.1840 \text{ joules.}$$

The results of the calibration experiments on the pentaborane system and the results of the pentaborane decomposition experiments are given in tables 3 and 4, respectively.

TABLE 3. *Results of the electrical calibration experiments on the pentaborane system*

Experiment	E	ΔP_c	E_s
	j	*Ohm*	*j/ohm*
1	48651.0	0.374654	129856
2	49904.1	.384457	129804
3	48058.8	.370289	129787
4	49314.9	.379834	129833
5	48547.3	.374191	129739
6	48495.9	.373680	129779
7	48657.3	.374996	129754
8	48529.6	.373886	129798
Mean			129794
Standard deviation of the mean			±14

TABLE 4. *Results of the pentaborane decomposition experiments*

Experiment	E	ΔP_c	q	q_s	q_c	B_5H_9	$-\Delta H$ (25° C)
	j	*Ohm*	*j*	*j*	*j*	*Mole*	*kj/mole*
1	49908.5	0.386650	50185.6	+0.4	−186.7	0.003409	54.77
2	49709.6	.384273	49876.3	−0.1	−166.8	.002889	57.74
3	49802.4	.385107	49984.6	+0.2	−182.0	.003560	51.12
4	49806.8	.385605	50049.2	+1.2	−241.2	.004353	55.41
5	49709.2	.385471	50031.4	+1.2	−321.0	.006037	53.17
6	51323.6	.397303	51567.5	+0.8	−243.1	.004508	53.93
Mean							54.36
Standard deviation of the mean							±0.91

The heats of decomposition obtained for the reactions of decomposition are given by the following equations:

$$B_2H_6(\text{gas})=2B(\text{solid, amorphous})+3H_2(\text{gas}),$$

$$\Delta H(25° \text{ C})=-6.73 \pm 0.52 \text{ kcal/mole,}$$

$$B_5H_9(\text{gas})=5B(\text{solid, amorphous})+9/2\ H_2(\text{gas}),$$

$$\Delta H(25° \text{ C})=-12.99 \pm 0.39 \text{ kcal/mole.}$$

The uncertainties assigned have been taken as twice the standard deviation of the mean of the experimental values, combined with reasonable estimates of all known sources of error.

By taking the amorphous form as the reference state of boron and 7.30 ±0.10 kcal/mole [9] for the heat of vaporization of pentaborane, the following heats of formation are obtained:

	ΔHf (25° C) kcal/mole
B_2H_6 (gas)	6.73 ±0.52
B_5H_9 (gas)	12.99 ±0.39
B_5H_9 (liquid)	5.69 ±0.40

4. Discussion

It was not possible to recover the finely divided boron quantitatively from the reaction vessel because of its tendency to adhere to the walls of the vessel as well as to the quartz wool plugs. It was therefore not feasible to obtain an accurate check on the completeness of the decomposition by determining the stoichiometric ratio between the masses of boron and hydrogen. In order to determine the presence of hydrogen, either chemically bound or adsorbed, samples of the boron produced were heated to 700° C in vacuum. Although traces of hydrogen were detected in some cases it is not likely that any significant error was introduced in the final result since the quantity of reaction in each case was based upon the mass of hydrogen evolved. Obviously, if all the boron-hydrogen bonds were of the same energy, the heat of decomposition as measured would be independent of the proportion of hydrogen removed in the process. The possibility that an extremely stable hydride was present was ruled out because portions of the residue treated with chlorine at 400° C were completely converted to boron trichloride [10]. The Constitution and Microstructure Section of the Bureau examined portions of the residue by X-ray diffraction methods. The absence of a pattern indicated that the boron was in an amorphous form.

In view of this information we conclude that the reaction of decomposition is quantitative and that the only products are amorphous boron and hydrogen. The thermal decomposition is probably the most convenient method for preparation of small quantities of high-purity boron.

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Temperature of the Inversion in Cristobalite

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The inversion temperature of cristobalite prepared from pure precipitated silica gel was compared with that of less pure cristobalite, including material derived from quartz. All materials showed a variability in their inversion temperature which was dependent on their thermal history. However, evidence suggested that a sufficiently extended heat treatment at high temperatures would in each case produce a uniform product with invariant inversion temperatures attributable to the low-high and high-low inversions. It is proposed that the variability of the inversion temperature can be rationalized in terms of three rate processes dependent on the temperature of heat-treatment, viz., nucleation, ordering, and crystal growth. The effect of all other factors known to influence the inversion temperature is either to accelerate or retard the rate of one or more of these processes.

1. Introduction

Cristobalite, the high temperature crystalline form of silica, undergoes a rapid,[1] reversible inversion from a low-temperature tetragonal structure to a gh-temperature cubic structure accompanied by a volume expansion of about 3.7 percent [1].[2] The inversion has been observed over a fairly wide range of temperature and is characterized by a hysteresis such that the inversion on cooling is invariably observed at a lower temperature than on heating. The peculiarities of the inversion have been investigated over a period of many years, but no clear understanding of the causes of the variation in the inversion temperature has been reached. Indeed, much conflict of opinion has been expressed both in and among reviews of the subject [2, 3, 4].

No precise agreement on the range of the inversion temperature exists, but recent investigators tend to quote values in the range of 200° to 280° C. However, the authors are not aware that a figure higher than 277° C has ever been observed. Moreover, because many of the systems studied have been neither homogeneous nor pure, it would seem more consistent to use a range extending from below 25° to 277° C, for cubic cristobalite has been shown to exist in opals even at room temperature.

The classical picture of the variability of the cristobalite inversion stems from the work of Fenner [5]. However, he raised many questions concerning the causes of the variability which still persist. Fenner investigated the possibility that the inversion temperature was dependent on the following variables: (1) Impurities within the material, (2) the thermal history of the material, (3) the source of the material (i. e., whether produced from quartz, tridymite, or amorphous silica), and (4) particle size. In recent years disorder within the structure has been added to this list. Furthermore, the postulation that more than one form of cristobalite exists has frequently recurred.

Fenner believed that impurities were not responsible for the variability, for he found a change in inversion temperature with heat treatment for cristobalite produced from quartz of 99.93 to 99.96 percent purity. More recently [6], however, an apparent double inversion in cristobalite has been associated with the presence of impurities, and the possibility in Fenner's work that the effect of impurities was masked by a larger effect due to the nature of the source material (quartz) should not be overlooked.

The temperature of formation of cristobalite is the variable most commonly associated with changes in its inversion temperature. Thus, Pierce and Austin [7] were able to show that the inversion temperature (from the thermal expansion curve) of cristobalite along the length of a used open-hearth furnace brick was almost linearly related to the temperature along the thermal gradient in the brick while in use. The higher the temperature at which the cristobalite was formed or heat treated, the higher was the inversion temperature.

The inversion temperature for the same heat treatment has been reported to be dependent, in some indefinite way, on the source of the silica. The experimental evidence is, however, again uncertain, for although Fenner reported that amorphous silica yielded a higher inversion temperature than quartz, Kondo, Yamuachi, and Kora [8] invariably found the opposite to occur. Various observers have noted that the state of subdivision of the quartz itself affects the rate at which cristobalite is formed,[3] but nowhere in the literature is it suggested that this fact alone makes direct comparison between the sources invalid on the "identical heat treatment" basis.

It is also invalid to associate changes in the particle size of the cristobalite with its inversion temperature, unless it is first shown that the particles are themselves the fundamental units undergoing inversion. In fact, no such association has yet been clearly demonstrated. Buerger [9], arguing from crystallographic concepts, has suggested that the correct variable in this context is crystallite size. If the crystallites are sufficiently small, then, clearly, a single particle may contain many of them. The surface of a crystallite, itself, represents a high degree of disorder and if the surface:volume ratio is high, a lowering of the inversion temperature may be expected. Flörke [10], from X-ray intensity considerations and dilatometric studies, has recently

[1] It is probable that this inversion is more accurately described as gradual-rapid. The high and low forms of cristobalite have not been identified by the letters α and β, since these symbols are employed ambiguously in the literature.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] The solid state transformation of any principal form of silica to any other principal form is always sluggish.

related the degree of crystallinity (extent of disorder) to the heat treatment and corresponding inversion temperature of various cristobalite samples. Cristobalite fired at lower temperatures had less sharp X-ray patterns, less marked expansion curves, and lower inversion temperatures.

Fenner speculated on the existence of more than one molecular species of cristobalite, and in 1926 Weil [11] reported two inversions (175° to 195° C and 217° to 245° C) in the same sample. More recently Plumat [12] has also noted an apparent double inversion, and Grimshaw, Westerman, and Roberts [13] reported the appearance and disappearance of two peaks in differential-thermal-analysis curves for a single sample subjected to successive heat treatments.

There have been very few attempts to associate any of the foregoing variables with changes in the hysteresis of the inversion temperature, even though the width of the hysteresis appears to be as variable as the inversion temperature itself. Unfortunately, a number of recent investigators have tended to record inversion temperatures for the low-high inversion only, hence there is less data available on the hysteresis. However, there appears to be no consistent support for the suggestion of Sosman [2, figure VII] that higher inversion temperatures yield wider hystereses. The only attempt known to the authors to explain the hysteresis on mechanistic principles is that of Mosesman and Pitzer [14]. They suggested that, on heating, a gradual rotation of the oxygen ions precedes the rapid alteration in bond length and direction. The rotation of the ions accounted for an anomalous rise in the specific heat before the rapid part of the inversion (accompanied by a latent heat effect) was observed. It may be postulated that, on cooling, the collapse of the structure from cubic to tetragonal symmetry cannot be effected until the rotation has ceased, and the inversion temperature on cooling is, therefore, lower than on heating.

In one of the reviews of the subject Dodd [3] concluded with the remarks: "It would seem that further research is needed based on very pure chemically precipitated silica subjected to controlled heat treatment under conditions precluding the possibility of contamination." It is very difficult to avoid minor contamination of powders at high temperature in any physically realizable furnace, but this investigation was an attempt to redetermine the cristobalite inversion temperature in accordance with Dodd's suggestion, and to compare the behavior of very pure cristobalite with less pure material including material derived from quartz.

2. Preparation and Purity of Materials

General qualitative spectrochemical analyses of the various materials used in the investigation are summarized in table 1. These are analyses of

TABLE 1. *General qualitative spectrochemical analysis of source materials*

Elements	Source material							
	Amorphous silica				Quartz			Commercial silica brick
	Gel from tetraethyl orthosilicate			Reagent silicic acid	Madagascar 1,500° C 4 hr	Near Lisbon, Md. 1,500° C 18 hr	Synthetic 1,500° C 24 hr	
	Lot A	Lot D	Lot E					
Ag	—	—?	FT	T	T	—?	T	FT
Al	—?	FT	T	VW	W	W	W	0.6%
B	—	—	—	T	—	—	—	VW
Ba	—	T	T	VW	—	VW	VW	VW
Be	—	—	—	—	—	—	—	VW
Ca	—	T	FT	T	VW	T	T	2%
Cr	—	FT?	—	FT?	T	FT?	FT?	T
Cs	—?	—?	—?	—	—	—?	—	—
Cu	FT	FT	FT	W	—	VW	M	M
Fe	—?	FT	—?	VW	VW	T	VW	0.3%
K	—	T	—	T	—	T	T	W
Li	—?	FT	—?	FT	—	FT	FT	T
Mg	FT	T	FT	FT	VW	FT	FT	W
Mn	—	—?	—	—?	FT	—?	—?	VW
Mo	—	—	—	—	—	W	VW	—
Na	—?	[a]VW	[a]VW	VW	—	VW	VW	VW
Ni	—	—	—	—	—	—	—	T
Pb	—?	FT	—	T	—	T	T	T
Rb	—	—?	—	—?	—	—?	—?	—?
Si	VS	VS	VS	VS	VS	VS	VS	VS
Sn	—	—?	—	—?	—	—?	—?	—?
Sr	—	—	—	—	—	—	—	W
Ti	—	—	—	VW	VW	VW	—	W
V	—	—	—	T	—	T	T	VW
Zn	—	—	—	W	—	—	—	W
Zr	—	—	—	VW	—	—?	—?	W
Estimated Purity % Min.	99.9998	[a]99.9854	[a]99.9876	99.7338	99.8579	99.7547	98.8547	95.4359
Estimated Purity % Max.	—	[a]99.99854	[a]99.99876	99.97338	99.98579	99.97547	99.88547	96.93359

NOTE: In general the following concentration ranges are indicated by the symbols: VS greater than 10%; S, 1-10%; M, 0.1-1%; W, 0.01-0.1%; VW, 0.001-0.01%; T, 0.0001-0.001%; FT less than 0.0001%; (—), not detected.

[a] Flame Photometer analysis for sodium indicated none present which was not also obtainable by a blank run. The sodium detected in the blank run amounted to 0.00157%. Quantitative spectrochemical analysis indicated less than 0.002%. It seems probable therefore that lots D and E were as pure as lot A.

source materials as received or as prepared, and the compositions may have been modified slightly by subsequent heat treatment. Furthermore, deliberate impurity additions were made to some samples.

Our highest purity material was prepared by the hydrolysis of redistilled tetraethyl orthosilicate. The resulting gel was prepared in five lots (designated Lots A to E), which were first heated overnight to 110° C to remove most of the water. The lots were then crushed lightly in an agate mortar and heated for 24 hr at 360° C to remove the last traces of alcohol.[4]

Various impurities were added to individual samples of lots B to E. These were added to the extent of 1 mole percent of the substances given in tables of results (table 5), with the exception of iron oxide for which there was no certainty as to its valency state in association with silica. Aluminum and germanium oxides were added directly as powders to the silica gel, iron was added as the oxalate, calcium as the carbonate or the phosphate, and the other elements as carbonates. All additions were intimately mixed with the silica gel as fine reagent grade powders before heat treatment.

The remaining samples of amorphous silica and quartz (table 1) were not subjected to any chemical treatment before conversion to cristobalite. An analysis of a typical unused commercial silica brick is given for comparison.

Samples were heated to form cristobalite by a uniform procedure. They were placed in covered platinum boats, and heated at a steady rate of 2°/min in a Pt-Rh wound mullite tube furnace until some preselected maximum temperature had been attained. The maximum temperature was held for a specified time to within ±5° C, whence the samples were cooled at 4° C/min until the temperature had fallen to about 700° C. At this temperature the natural cooling rate of the furnace became less than 4°/min and the samples were permitted to cool at the natural rate to room temperature over a period of 12 to 24 hr.

After heat treatment the samples were ground to a fine powder (through a 200-mesh screen) with an agate pestle and mortar. The particle size distribution of these powders was not determined.

Minor deviations from this general method of preparation were followed with a few samples in order to study special effects, or because of the limited quantity of source material available. Such deviations are given in the sections 4 and 5 (Results and Discussion) when the inversion temperatures of such samples are discussed.

3. Apparatus and Experimental Procedure

In recent years both X-ray and differential thermal analyses have been added to the earlier optical and thermal expansion methods of studying the inversion. Both methods of analysis were used in this investigation, and the results were supplemented by observations with a hot-stage microscope and an electron microscope.

Differential thermal analysis (DTA) is a particularly useful routine technique and has been employed throughout this investigation. Both the theory of the technique and its application to the cristobalite problem have been recently reviewed [15], and will not be described in detail here. Grimshaw and Roberts [13, 15], and others, have reported that they were unable to obtain reliable inversion temperatures on cooling by the DTA method. However, in this investigation it was found that, by using a specially designed furnace, reliable inversion temperatures could be obtained both on heating and cooling.

Figure 1 shows the all-copper furnace which was constructed for the DTA apparatus. The furnace was intended for use only up to 300° C, and no difficulty with the oxidation of the copper was experienced if this temperature was not exceeded. Reproducible and uniform heating rates could usually be obtained using a manually controlled variable transformer. The furnace was allowed to cool naturally, with the heater power turned off. The rate of cooling could be varied by changing the furnace insulation, or by surrounding the furnace with a cold jacket. The cooling curve thus obtained was not, of course, a straight line over wide ranges of

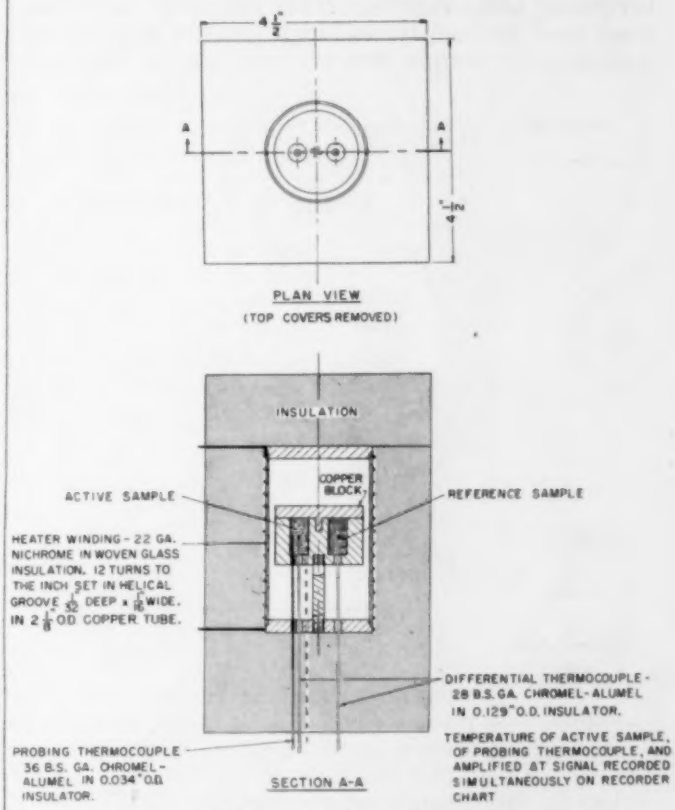
4½"
A
A
PLAN VIEW
(TOP COVERS REMOVED)
INSULATION
COPPER BLOCK
ACTIVE SAMPLE
REFERENCE SAMPLE
HEATER WINDING - 22 GA. NICHROME IN WOVEN GLASS INSULATION. 12 TURNS TO THE INCH SET IN HELICAL GROOVE 3/32 DEEP x 1/16 WIDE, IN 2 1/8 OD COPPER TUBE.
DIFFERENTIAL THERMOCOUPLE - 28 B.S. GA. CHROMEL-ALUMEL IN 0.129" O.D. INSULATOR.
TEMPERATURE OF ACTIVE SAMPLE, OF PROBING THERMOCOUPLE, AND AMPLIFIED ΔT SIGNAL RECORDED SIMULTANEOUSLY ON RECORDER CHART
PROBING THERMOCOUPLE 36 B.S. GA. CHROMEL-ALUMEL IN 0.034" O.D. INSULATOR.
SECTION A-A

FIGURE 1. *Differential thermal analysis furnace.*

Alternative position of probing thermocouple shown with broken lines. The drawing is to scale. The insulation consists of cut sections of Class 28 insulating brick.

[4] The prolonged, low-temperature heat treatment was necessary for the removal of alcohol without decomposition to a black carbonaceous deposit. Once formed the deposit could only be removed by prolonged heat treatment even at 1,550° C.

temperature, but could be approximated to a straight line over the limited range in which the inversion occurred. In the normal routine analysis of samples the insulation was as shown in figure 1 and yielded a cooling rate of about 4° C/min through the inversion range. The heating rate was, then, also set to approximate this figure.

As discussed in the following section (Results), it was found, rather surprisingly, that varying the heating and cooling rates gave significant changes in the temperatures at which peaks occurred in the differential-temperature (ΔT) curve. The figure of 4° C/min represented a compromise which gave relatively high peaks which were yet broad enough to give fair details of the singularity or multiplicity of their structure. Very slow rates were difficult to control with precision, while rapid heating and cooling tended to smear out significant differences in inversion temperature within a sample.

4. Results

4.1. Differential Thermal Analysis

Some traces of DTA records of particular interest are shown in figure 2. The bulk of the DTA results are, however, best presented in tabular form and are given in the sequence of tables 2 through 7.

In interpreting the data from the ΔT curves it has been assumed that peaks in these curves represent inversion temperatures. The difficulty here has been that frequently no single peak was obtained with a given sample, nor yet just two (as has been previously reported in the literature [13]). In fact, certain samples persistently gave so many peaks that it was difficult to resolve these from a continuous hump in the ΔT curve. There was abundant evidence that when two peaks occur close together one peak influences the apparent inversion temperature indicated by the other. The situation was further complicated because samples which gave very sharp, high peaks on heating through the inversion temperature often gave very skewed, double or even treble peaks on cooling. Except in cases where there was a definite skew in the peak obtained on heating, it was not possible to resolve the one peak into two identifiable peaks. The suggestion remained that the character of the inversion on heating was different from that on cooling. This suggestion was supported both by the readiness with which the inversion temperature on cooling was subject to variations not attributable to further high-temperature heat treatment, and by the fact that inversion temperatures on cooling were subject to greater fluctuations than inversion temperatures on heating.

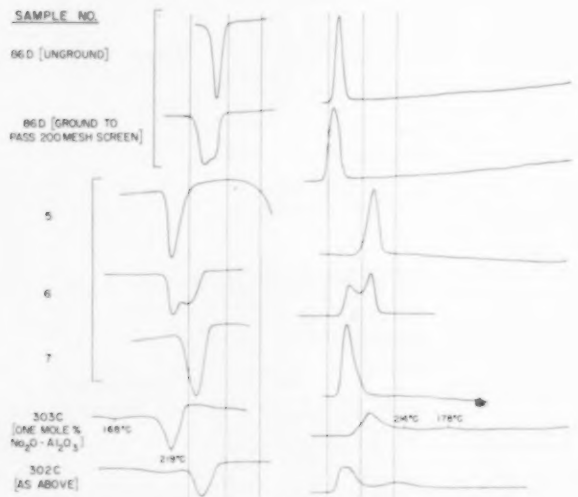

FIGURE 2. *Traces of typical differential temperature curves on heating and cooling at approximately 4° C/min.*

TABLE 2. *DTA of samples prepared from tetraethyl orthosilicate*

Sample No.	Peak temperatures obtained by heating and cooling at 4° C/min after stated heat treatments					
	Heat treatment		Heating		Cooling	
	Maximum temperature	Time	Peak temperature	Peak height	Peak temperature	Peak height
	°C	hr	°C		°C	
33A	1,200	6	[a]	[a]	[a]	[a]
37B		24	[a]	[a]	[a]	[a]
55B		48	225?	------	205–15?	------
82D		192	253	74	221	59
					229	35
84D		384	242	22	215	28
			251	62	222	63
39	1,250	12	[a]	[a]	[a]	[a]
43B		192	254	140	229	104
32A	1,300	6	254–5	6	227	10
36B		12	255	46	232	41
38B		96	257	129	227	91
					232	95
40B		192	257	143	232–3	143
45B	1,350	6	[b]	[b]	[b]	[b]
46B		12	256–7	34	230	24
					233	27
47B		48	261	128	237	126
48B		96	260–1	132	236	124
49B		192	262–3	142	238–9	134
50B	1,375	6	258	6	232–3	5
53B		7½	258–9	50	236	46
52B		9	260	26	235	25
					228	19
54B		10½	257	27	234	24
51B		12	266	135	240	128
31A	1,400	6	266	157	241	148
57D		12	266	178	234	89
					241	92
59D		96	266	196	225	53
					241	94
79D		192	266	197	235	70
					240	82
81D		408	266	207	224	40
					240	86
30A	1,500	6	268	184	242	175
78D		96	269	215	238	68
					243	96
35B	1,550	6	268	179	243	179
83D		48	270	212	238	103
					244	106
34B	1,600	6	267–8	187	242	181
56B	1,650	6	270	172	236	101
					244	171
86D	1,700	18	272	174	235	122
					241	111

[a] No observable peaks.
[b] No measurable peaks.

TABLE 3. *DTA of samples prepared from reagent silicic acid*

Sample No.	Peak temperatures obtained by heating and cooling at 4° C/min after stated heat treatment									
	Heat treatment		Peak 1				Peak 2			
	Maximum temperature	Time	Heating	Height	Cooling	Height	Heating	Height	Cooling	Height
	°C	hr	°C		°C		°C		°C	
14	1,100	3	238	110	211	115	----	----	----	----
16		6	234–5	97	209–10	103	----	----	----	----
17		12	235	75	210	96	----	----	----	----
13	1,200	3	243	87	214–5	90	----	----	----	----
5		6	241	101	214	105	----	----	----	----
15		12	241–2	67	215–6	82	----	----	----	----
18		24	234–5	94	209	103	----	----	----	----
20		48	235	89	210	90	----	----	----	----
26		192	244	37	216	34	252	119	225	119
28		384	(a)	(a)	220	96	251	129	228	67
11	1,300	3	242–3	52	215–6	59	259	48	227	48
6		6	243	60	215–6	63	259	43	225	49
12		12	242	60	215	59	259	51	226–7	47
19		24	242–3	49	214–5	53	258	53	226–7	49
21		48	242	39	215	39	259	61	227–8	51
9	1,400	3	242–3	50	216	55	260	51	229	46
3		6	241	157	214	157	----	----	----	----
10		12	242–3	51	216–7	59	260	44	227	43
24		192	----	----	----	----	269	135	235 239	81 83
25		408	----	----	----	----	267	125	224 238	39 75
2	1,500	6	249–50	86	222	97	259	41	(b)	(b)
1		12	257–8	72	228–9	92	262–3	107	233–4	89
7	1,550	6	----	----	----	----	261	107	230	99
27		48	----	----	----	----	270	129	237 244	63 93
8	1,600	6	----	----	----	----	264	150	235–6	128

[a] Merged into Peak 2.
[b] Merged into Peak 1.

TABLE 4. *DTA[a] of samples produced from quartz*

Heat treatment		Peak temperatures °C (Peak heights shown in parentheses)					
		Madagascar		Near Lisbon, Maryland		Synthetic	
Temperature	Hours	Heating	Cooling	Heating	Cooling	Heating	Cooling
1,400	6	----	----	----	----	230 (41)	221 (42)
1,500	4	238 (90)	218 (83)	----	----	----	----
	6	----	----	----	----	227 (81) 247 (10) 265 (3)	219 (83) 231 (13) 241 (3)
	12	----	----	240 (59) 246 (84)	227 (77) 231 (94)	----	----
	18	----	----	242 (78) 246 (99)	----	----	----
	24	----	----	----	----	232 (87) 249 (11)	216 (100) 230 (13)
1,600	6	252 (91)	227 (101)	----	----	257 (131)	234 (126) 243 (23)
	12	264 (156)	233 (92)	----	----	262 (163)	236 (116) 244 (24)
	18	264–5 (172)	232 (77)	----	----	262 (160)	237 (106) 242–3 (20)
	24	265–6 (180)	233–4 (77)	----	----	----	----
1,700	24	----	----	----	----	272 (142)	233[b] (116)

[a] DTA heating and cooling rate 4° C/min.
[b] Second peak merged into this at about 239° C.

Further comment on these observations will be given subsequently, both in this section and the following Discussion (section 5). First, however, some comment on the validity of identifying peak temperatures with inversion temperatures is warranted.

Apart from a consideration of the significance of the peaks as fundamental reference points, it is pertinent to question whether the peaks occurred at invariant temperatures for given samples. With the equipment used in this investigation the temperatures at which peaks occurred were reproducible to within less than ½° C for fixed heating (or cooling) rates. However, peak temperatures could be raised 7° to 8° C by increasing the heating rate from ⅛° to 35° C/min. Rapid cooling lowered the peak temperatures or suppressed higher temperature peaks

TABLE 5. *DTA of samples containing one mole percent of added impurities*

Impurity	Peak temperatures obtained by heating and cooling at 4° C/min from samples heated for 6 hr at stated temperatures (Peak heights in parentheses)									
	1,200° C		1,400° C		1,500° C		1,600° C		1,650° C	
	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling
None	None	None	266 (157)	241 (148)	268 (184)	242 (175)	268 (187)	242 (181)	270 (172)	236 (61) 244 (109)
Al_2O_3					260 (92)	224 (58) 228 (63) 241 (18)	263 (122)	239 (127)	261 (116)	238 (117)
Na_2O			116 (6) 162 (1) 264 (73)	233 (49) 239 (51)	116 (3) 259 (89)	235 (75) 242 (63)	116 (2) 268 (100)	239 (81) 244 (90)		
$Na_2O \cdot Al_2O_3$	[b] 178 (3) 214 (2) 242 (25)	167 (4) 219 (62)	214 (16) 220 (14) 229 (12) 256 (9)	190 (13) 202 (25) 214 (15) 232 (7)	250 (40)	224 (46)	214–223 (6) 258 (31) 263 (34)	206–213 (3) 234 (44)		
MgO	None	None	255 (103)	226 (69) 232 (51) 238 (36)	263 (156)	238 (115)	264 (181)	240 (152)		
Fe_xO_y [a]	None	None	252 (126)	222 (67) 226 (56) 241 (18)	255 (137)	225 (44) 233 (70) 242 (28)	265 (184)	234 (72) 239 (146)		
Li_2O	116 (3) 173 (1) 246 (46)	223 (71)	116 (13) 171 (1) 262 (37)	233 (37) 238 (33)	115 (2) 266 (87)	237 (70) 243 (81)	117 (1) 263 (30) 272 (116)	238 (92)		
CaO			245 (74) 258 (13)	221 (62) 227 (55)	264 (122)	230 (101)	268 (159)	234 (98) 242 (85)		
$Na_2O \cdot Fe_2O_3$			247 (46) 249 (42)	218 (69) 240 (4)	249 (53) 258 (39)	226 (51) 233 (68)				
$CaO \cdot Al_2O_3$			232 (22) 236 (25) 254 (6)	208 (37) 226 (10)	240 (20) 245 (19) 263 (3)	209 (35) 218 (21) 228 (9)	198 (9) 254 (23) 265 (7)	188 (7) 229 (36)		
BaO			247 (70) 260 (15)	218 (56) 240 (15)	255 (36) 258 (36)	230 (87)	270 (175)	243 (147)		
K_2O			117 (8) 263 (70)	232 (65)	272 (109)	237 (120) 243 (62)	272 (115)	243 (124)		
$Ca_3(PO_4)_2$					258 (113) 268 (33)	233 (85) 239 (56)	268 (126)	239 (114)		
GeO_2					270 (141)	244 (128)				
$Al_2O_3 \cdot Ca_3(PO_4)_2$					237 (21) 242 (22) 257 (32) 261 (33)	215 (52) 228 (34) 237 (20) 244 (23)				
$Li_2O \cdot Al_2O_3$					258 (57)	233 (78)				
$K_2O \cdot Al_2O_3$							241 (9) 265 (32)	219 (11) 236 (38)		
$MgO \cdot Al_2O_3$							251 (84) 266 (37)	230 (105)		
$BaO \cdot Al_2O_3$							238 (?) 255 (47)	224 (75)		

[a] Added as 2½% by weight of $FeC_2O_4 \cdot 2H_2O$.
[b] Heated 192 hr.

TABLE 6. *DTA of samples prepared from gel of different particle sizes*

Mesh size of gel		Peak temperatures obtained by heating and cooling at 4° C/min for stated heat treatments											
		Heated at 1,450° C for 6 hr							Heated at 1,600° C for 6 hr					
		Sample no.	Heating		Cooling				Sample no.	Heating		Cooling			
Through	On		Temperature	Height	Temperature	Height	Temperature	Height		Temperature	Height	Temperature	Height	Temperature	Height
			°C		°C		°C			°C		°C		°C	
325	-----	60D	259	130	227	98	-----	-----	74D	267	165	-----	-----	[a] 240	119
200	325	62D	263	153	229	111	-----	-----	73D	267	169	-----	-----	238	108
140	200	65D	266	146	231	[a] 99	-----	-----	72D	268	173	230	70	241	121
100	140	69D	267	160	231½	90	242	88	71D	266	167	230	85	240	98
80	100	64D	265	153	232	92	240	75	70D	266	181	233	63	242	155
40	80	63D	264	182	234	39	242	176	68D	267	221	-----	-----	245	210
20	40	61D	263	162	-----	-----	241	149	67D	267	192	-----	-----	244	191

[a] These peaks markedly skewed in direction of other cooling peaks.

TABLE 7. *X-ray determination of inversion temperatures by change of structure*

Sample 67D[a]		Sample 71D[a]	
Temperature	Structure	Temperature	Structure
° C		° C	
Heating:		Heating:	
255–6	Tetragonal.	256	Tetragonal.
261	Cubic and small amount of tetragonal.	264	Cubic.
264	Cubic.		
Cooling:		Cooling:	
234	Cubic and trace of tetragonal.	231	Tetragonal and cubic.
225	Cubic and small amount of tetragonal.	226	
219	Tetragonal and trace of cubic.	220	Tetragonal.

[a] History of these samples is given in Table 6. The authors are indebted to W. Johnson and K. W. Andrews of the United Steel Cos., Central Research Laboratory, Rotherham, England, for making these determinations.

in favor of lower temperature peaks. The heating and cooling rates used for the routine analysis (4° C/min) gave peak temperatures which were about 2° C higher (or lower) than those obtained by the slowest rates. The exact error involved in passing through the inversion rapidly was difficult to determine, however, because of the multiple peak character of the ΔT curve for many of the samples.

For rapid, reversible inversions the recorded inversion temperature should be independent of the heating rate and identical with the temperature of a peak in the ΔT curve [15, 16, 17] (providing the thermocouples are located at the center of the specimens). Cristobalite is a substance whose individual crystallites may all have rapid inversions, but not identical inversion temperatures. Although the individual inversions take place only over a limited range of temperature, it is possible that the temperature at which the peak in the ΔT curve occurs may be fortuitous and dependent upon the distribution of the inversion temperatures among the crystallites of the sample. It was observed on a hot-stage microscope that all the crystallites of a sample do not, in fact, invert at the same temperature. (See also the paper by Chaklader and Roberts [18]). It has been suggested by Hargreaves [5] that, as an alternative to using the peak temperature, the temperature at which the ΔT curve first deviates from its base line yields a temperature more characteristic of a sample. With the apparatus and samples used in this investigation this temperature was 5° to 20° C lower than the peak temperature on heating, and in order to justify its acceptance it was necessary to determine whether the temperature gradient through the samples was negligible by comparison. An additional probing thermocouple was inserted into the outside of the cristobalite as shown in figure 1. The temperature registered by this thermocouple was then recorded on a chart along with the usual DTA data. It was thus possible to observe the temperature at which the ΔT curve first departed from its base line simultaneously with the temperature of the probing thermocouple (fig. 3). By this method it was possible to show that the initial departure of the ΔT curve from its base line was associated with temperature gradients in the sample, rather than with variations in the inversion temperature (fig. 3). The different inversion temperatures were fairly uniformly distributed throughout the samples. It was thus concluded that the peak in the ΔT curve provided the best estimate of the inversion temperature of a sample as a whole, notwithstanding the observation that no single temperature could be given for all the individual crystallites. Furthermore, it was, in general, desirable to correct for the significance of heating rates in converting observed peak temperatures to estimated inversion temperatures.

During the course of the investigation, it was observed that there were three extraneous factors involved in the experimental procedure which were sometimes significant in determining the inversion temperatures indicated by DTA. It appeared possible that peak temperatures could be changed

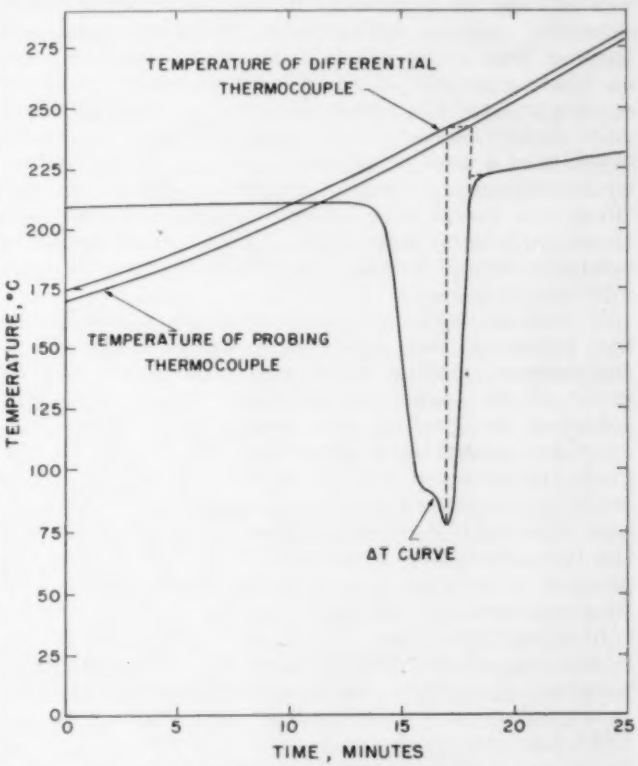

FIGURE 3. *Trace of a typical recorder plot of a cooling curve, showing that the initial departure of the differential temperature (△T) curve from its base line can be associated with a temperature gradient within the sample.*

The temperature gradient within the sample is shown by the different temperatures of the differential thermocouple (located in the center of the sample) and the probing thermocouple (located at the edge of the sample) at particular times.

[5] Private conversation. We are indebted to Dr. J. Hargreaves (Research Laboratories of United Steel Companies, Rotherham, England) for first suggesting these possibilities. He has further noted that with samples he has prepared, the hysteresis in the inversion temperature is eliminated if this alternative criterion is employed. Within ±2° C (the error being largely due to the difficulty of locating the precise temperature at which the ΔT curve departs from its base line) many of the heating and cooling curves resulting from this investigation also show this effect (at about 250° C). The effect is, however, not consistent (and probably quite fortuitous). Hargreaves also found, however, that by using this criterion he was able to reconcile inversion temperatures determined by DTA with those obtained by Johnson and Andrews by X-ray methods [1].

(1) by quenching samples from high temperature following heat treatment, (2) by grinding the samples in the agate mortar after treatment, and (3) by cycling samples through the inversion in the DTA furnace.

The first factor was taken care of in the experimental procedure by cooling samples at a controlled rate. The effect of quenching a sample from high temperature was, however, investigated using a portion of sample 79D (table 6). The peak temperatures obtained were not significantly different from those of the unquenched sample (70D), but there was some small difference in the relative heights of the peaks obtained on cooling.

The data given in the tables of results are not corrected for the heating rate because of the difficulty of knowing the exact correction for each sample. In any case, the error involved with many of the samples is believed to be slight. The peak heights are given in arbitrary units, intended merely to indicate their relative heights.

It was not discovered until most of the samples had been analyzed that the process of grinding the samples for DTA had a significant effect on the peak temperatures obtained. The effect during heating was slight and barely detectable in most instances. However, there was good evidence that the second (lower temperature) peak obtained during cooling was at least in part attributable to grinding. For example, sample 86D (table 2) when analyzed without first being crushed or ground gave a peak on heating at 270° C, and a single sharp peak on cooling at 244° C. Successive crushing and grinding only slightly raised the heating peak but gradually introduced a new lower temperature peak on cooling which ultimately became dominant (fig. 2). This effect was noted with other samples, but not with those containing impurities. The results given in the tables are all for samples crushed to pass through a 200-mesh sieve.

The third factor observed was the antithesis of the foregoing, for with some samples the lower temperature cooling peak could be eliminated in favor of the higher temperature peak. This was achieved by cycling the temperature about the inversion points and observing the change in the peak temperature during successive cycles. The lower temperature peaks of samples 70D, 71D, and 72D (table 6) could all be eliminated by cycling the temperature in this way. However, it was not possible to remove the skewness from sample 74D by this technique. Moreover, when cycling samples containing impurities, only a slight effect was noted, which was of doubtful significance. The peak temperatures given in the tables of results are for samples subjected to a single heating and cooling in the DTA furnace.

4.2. X-Ray Analyses

The purpose of the X-ray analyses was twofold. First, an attempt was made to check the inversion temperature against observed changes in crystal structure; second, samples with different inversion temperatures were examined at room temperature for variations in inherent structure, order, and crystallite size.

The results of the inversion temperature determinations are given in table 7. It will be noted that there is a difference in the inversion temperatures as indicated by X-ray analysis and DTA. Because, however, there is an inherent difficulty of accurate temperature measurement in most high-temperature X-ray cameras, this lack of agreement is probably of little significance. Of perhaps greater significance is the range of temperature over which the inversion occurred, although, here again, some of this range may be due to temperature gradients within the sample.

The results of the structure and crystallite size investigations were deduced from counter diffractometer traces obtained by scanning over the angular region $2\theta = 5°$ to 162°. The studies were made at room temperature using samples 35B (DTA peak 268° C), 43B (DTA peak 254° C), and 9 (DTA peaks 242° and 260° C). No appreciable differences in low angle scattering ($\theta = 5°$ to 11°) were observed, indicating a crystallite size greater than 10[illegible] in all samples. Likewise, no significant differences in diffraction line intensities or peak positions were detected, suggesting identical or very closely similar atomic packing in the crystallite regions. Shifts in the X-ray diffraction patterns of the type described by Flörke [10] were, therefore, not a prominent feature of any sample. The width of the diffraction lines, however, varied markedly between the samples, especially at high angles.[6] The line profiles of sample 43B were wider than those of sample 35B throughout the scanning range, the high-angle peaks being very diffuse (fig. 4). The line broadening for the latter sample was very little more than that attributable to the experimental technique, indicating crystallites of size larger than 1000 A and of small internal strain. Attempts to

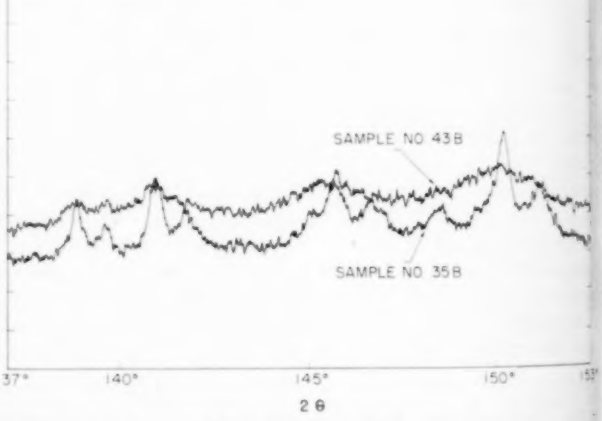

FIGURE 4. *X-ray diffraction line intensities for the angular region $2\theta = 137° - 153°$.*

Sample 43B gave a DTA peak at 254° C during heating, and sample 35B gave a DTA at 268° C.

[6] In Flörke's investigation [10] the diffraction patterns are shown only for low angles.

obtain the causes for the line broadening were based on a number of assumptions, none of which were fully justified, and whose cumulative errors precluded any reliable quantitative interpretation. Nevertheless, the following qualitative conclusions were almost certainly justified.

(a) The rate of broadening with Bragg angle was too great to be solely attributable to the small crystallite size in sample 43B. Significant crystallite strains appeared to exist.

(b) The ultimate crystallite size was likely to be of the order of 50A.

(c) The results for sample 9 were similar to those for sample 43, with the possibility of a wider crystallite size distribution.

5. Conclusions and Discussion

The results of the investigation even with the very pure material retain a certain lack of reproducibility and definitude. The lack of reproducibility was clearly inherent both in the nature of the samples (they were not homogeneous with respect to inversion temperature) and the experimental procedure, and even the most meticulous use of the techniques used in this investigation could hardly eliminate it. Some greater definitude in the results might have been obtained if samples had been heat treated longer, whereas now probable trends alone are indicated. It is, however, possible to draw a number of conclusions which appear justified by the results.

It is clear that the most important variable associated with variations in the inversion temperature is the time and temperature of heat treatment. In order to provide some cohesion to a discussion of the variability of the inversion temperature in general, it is first proposed that the actual inversion temperature of the crystallites can be associated with three rate processes dependent on the temperature of heat treatment. These processes are, first, nucleation of the cristobalite phase from the source material; second, an ordering effect whereby small, well-ordered, strain-free crystallites are developed; and last, grain growth from the well-ordered crystals. That, within a polycrystalline sample, there will be an interplay between these processes is obvious. The result of each process will be a net loss of energy of the system and an observed increase in the inversion temperature. It is believed that a careful study of the effect of heat treatment upon the inversion temperature over the range 1,100° to 1,700° C supports the conclusion that there are three stages involved.

Consider the temperatures obtained for the low to high inversion with the samples prepared from tetraethyl orthosilicate (table 2). (The high to low inversion will be discussed subsequently.) Up to 1,350° C, very little cristobalite was formed during short-term heating (6 to 12 hr), but there was evidence that freshly nucleated material in an amorphous matrix inverted at temperatures around 225° C. It is believed that the general concept of a temperature-dependent rate process for nucleation will be readily accepted without detailed argument, but the question of whether nucleation occurs at a surface or within the gel may still be a matter for speculation.

Following nucleation, further heat treatment yields a progressive increase in the inversion temperature until this reaches 266° C. The rate at which the inversion temperature increases is temperature-dependent; heat treatment at 1,200° C for 384 hr causes the inversion temperature to rise only to 251° C, whereas at 1,375° C heat treatment causes the inversion temperature to reach 258° C after 6 hr and 266° C after 12 hr. It appears that the attainment of an inversion temperature of about 266° C represents the completion of the second process, whereby the freshly nucleated material develops well-ordered, strain-free crystallites.

It was observed that the inversion temperature of 266° C was attained after only 6 hr heat treatment at 1,400° C, but that more extended heat treatment at this temperature (up to 408 hr) did not raise the inversion temperature further. Heat treatment at higher temperatures, however, yielded a further slow rise in the inversion temperature, the rate of rise again apparently increasing with the temperature of heat treatment. The highest peak temperature obtained by DTA of this material was 272° C, but it is not unlikely that more prolonged heating at high temperatures would raise the inversion temperature somewhat further. That the slow rise in inversion temperature can be associated with a rate process is clear, but it must be admitted that the proposal that the process is crystal growth is based on little more than speculation. The proposal does, however, seem a reasonable possibility and is in at least qualitative accord with the known slow growth of cristobalite crystals.

From the above broad proposal it is possible to suggest the effect of particular variables on the inversion temperature. It is suggested that the general effect of impurities, the source material, and the crystal or particle size is merely to vary the rate of the above processes. For it appears that all cristobalite, from whatever source, and of whatever purity, will ultimately invert at the same temperature if subjected to a sufficiently extended heat treatment.

As far as rates are concerned, however, the effect of even relatively small amounts of impurity are significant, for the inversion temperatures of the cristobalite prepared from reagent silicic acid (table 3) are significantly different from the results discussed above. First, it will be observed that the impurities which were present in this material accelerated the nucleation of the cristobalite, since cristobalite was formed in only 3 hr at a temperature as low as 1,100° C. However, they retarded the ordering process yielding DTA curves very typical of the "two-peak" type which have been reported before. Nevertheless, the end product of heat treating this material appears to be identical with the end product from tetra-ethyl orthosilicate. Indeed, it is striking that two materials can yield cristobalite samples which behave so differently

after low-temperature heat treatment, yet which are indistinguishable after high-temperature treatment.

The effects of the deliberate impurity additions (table 5) were in general accord with the above remarks, but were more complex. With some impurities the attainment of a relatively stable end product was retarded, and with others accelerated. We did not obtain any evidence that the end product of samples containing impurities was any different from that of the pure materials. Hence one may be justified in concluding that cristobalite rejects impurities in its structure during heat treatment at high temperature. The alkali ions Na, Li, and K each produced small DTA peaks which were attributable to tridymite, but these peaks were not detected with any other impurity. We have not attempted to relate the size or valency of the impurity ions to the magnitude or sign of their effect on the proposed rate processes. At this stage speculation alone can suggest whether some of these would occupy interstitial sites in the silica structure, substitute themselves for the cation, merely attach themselves to the surface, or enter into new polycomponent systems. It may be significant, however, that the $Na_2O \cdot Al_2O_3$ and $CaO \cdot Al_2O_3$ impurities contributed a larger effect than any other variable studied, because aluminum plus an alkali or alkaline earth is known to substitute for silicon in the silica structure. These impurities contributed DTA peaks as low as 178° C, but the possibility exists that some of the peaks may be more properly attributed to impurity stabilized phases within the silica matrix. It should not be overlooked that tridymite itself may fit into this category.

A further important effect of the impurities concerns the number of DTA peaks obtained. It will be observed (table 2) that the single peak character of the inversion was characteristic of the very pure material, with the exception of one sample prepared at low temperatures. (We are still discussing the low-high inversion only.) On the other hand, impure specimens tended to give a multiplicity of peaks which at times became difficult to resolve from a continuous hump spread over 20° to 40° C. There seems to be no sound reason for interpreting these peaks in terms of a number of different forms of cristobalite, unless substantial supporting evidence is produced. It would appear to be more probable that the appearance and disappearance of these peaks is associated with a lack of homogeneity within the sample in terms of the rate processes previously described. The multiple peak character of the DTA curves can be attributed to a tendency for groups of crystallites within particular samples to reach distinct stages of development. Since impurities most commonly slow down that process following nucleation to which the inversion temperature is most sensitive, the spread of inversion temperatures should become more apparent. And it is with just those impure samples in which the ordering process proceeds most slowly that the multiple peaks are most obvious.

It should be clear, in terms of a rate process interpretation of the variability of the inversion temperature, that cristobalite produced from quartz is not going to give the same inversion temperature as ge for the same heat treatment, unless identical end products have been obtained. Before cristobalit can be nucleated from quartz, there has to be a breaking of bonds within the structure, and this is energetically speaking, a more difficult and time-consuming process than is encountered with the gel. Our results are in accordance with this expectation. In addition, the result of heating quartz to 1,700° C for 24 hr suggests that the end product obtained is identical with that obtained from gel.

We turn now to a consideration of the high-low inversion. It has already been stated that the nature of the inversion on cooling indicated by DTA was different from that on heating. The question may, however, be asked: was there a *real* difference, or were the observations merely inherent in the experimental procedure?

It is believed the difference was real, first, because observations were apparently independent of such variables as the DTA heating rate which would be most likely to yield anomalies of this type. The probing thermocouple did not indicate that the magnitudes of the temperature gradients on heating were significantly different from those on cooling. Secondly, the X-ray data (table 7) also suggested that the inversion on cooling was spread over a wider temperature range than on heating. Thirdly, the inversion on cooling appeared susceptible to significant variations independent of any observable variation on heating. Furthermore, if the inversion is accepted as being of the gradual-rapid variety on heating it may, nevertheless, only be of the rapid variety on cooling. It may well be that the rapid inversion of the high form is retarded until such time as sufficient energy of rotation of the oxygen ions has been lost that all the structural changes within a crystallite can be effected at the same time.

On the basis of this interpretation it is possible to suggest why two DTA peaks were obtained on cooling when only one peak was obtained on heating. It may be postulated that, on cooling, DTA is more sensitive to small structural inhomogeneities (such as strain induced by grinding) within the sample. That is, that inhomogeneities which are smeared out by the gradual onset of rotation on heating are nevertheless observable on cooling. More exact heat-content data would be required to test this interpretation.

Apart from the general anomalies obtained for the high-low inversion, the variability of the inversion temperature was generally consistent with proposals given for the low-high inversion. There was a suggestion in the data that more prolonged heat treatment at higher temperatures was redeveloping the lower temperature peak at the expense of the higher temperature peak. However, no ready explanation could be found as to why the peak temperature gradually rose to about 244° C and then fell off with the development of the lower temperature peak, unless the more extensive heat treatment yielded samples

which required more grinding and thus were subjected to greater strain.[7]

The lack of homogeneity within samples, the limitations of DTA techniques, and the anomalies obtained for the high-low inversion make an unequivocal identification of the temperatures of the inversion very difficult. Assuming that very slow heating rates yield a more accurate correspondence between peak temperatures and truly representative inversion temperatures, but that further heating of our samples would have slightly raised our peak temperatures, the best estimate we can give for the low-high inversion is 270° to 272° C. This value is for samples of well ordered, well developed crystals, and is somewhat lower than previously proposed maxima. Complete information on the heating rates used to determine inversion temperatures has not always been given in the literature. Indeed, it has been supposed that indicated inversion temperatures are independent of heating rates. In many instances, however, heating rates of 15° C/min and greater have been used and it seems probable that apparent inversion temperatures in the range 270° to 280° C are attributable to rapid heating rates. In this investigation it has been possible to obtain similar values by the use of rapid heating rates with samples which yielded peak temperatures of 272° C or lower during slow heating.

Similar considerations are pertinent to the identification of the temperature of the high-low inversion, although, in this case, we also have to contend with the anomalous multiple peak character of the inversion. Neglecting effects which are believed to be partially due to grinding, it appears that the inversion on cooling is about 26° C lower than on heating, yielding a value of 244° to 246° C.

The authors thank H. S. Peiser of the Bureau for his contributions to the understanding of the structural variations of our samples as indicated by X-ray analysis. David C. Ailion, now a graduate student at the University of Illinois, also assisted with the preparation of the pure silica samples and with the routine differential thermal analysis.

[7] The persistence of a single, often skewed, low temperature peak at about 233° C was also common with samples derived from quartz.

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Infrared Emission Spectra of Flames Under High Resolution[1]

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The spectrum of a hydrogen-oxygen flame and an oxyacetylene flame has been measured in the near infrared region with a high-resolution grating spectrometer. In the region from 3.7 to 4.1 μ many lines are observed which have not been classified. They may arise from transitions belonging to the ν_2 or ν_3 bands of water vapor. The intensity of the first overtone band of CO was increased when a high-frequency discharge was passed through the flame and the infrared CN band was increased in intensity when N_2O was mixed with the acetylene. The results are shown in five figures of the observed spectra.

1. Introduction

There have been a large number of researches on the infrared emission of flames in the last 10 years, but investigations in this field extend back to the early period of infrared spectroscopy. In 1890 Julius [1] [2] measured the radiation from flames in which various fuels were used. When CS_2 was used as a fuel, he observed that the strongest bands in emission occurred at the same wavelengths as the bands which were present in the CS_2 absorption spectrum. The emission specturm of H_2O and CO_2 was extensively studied by Paschen [2] and by Rubens and Aschkinass [3]. They observed the shift of the maximum of emission in CO_2 from 4.27 to 4.40 μ with increasing temperature of the flame.

With the improved present-day optics and detectors in grating spectrometers many of the infrared emission bands can be resolved sufficiently to show the rotational lines in the bands, and weak bands can be observed which were not discerned by prism spectrometers. Previous reports [4] have given the measurements on the spectra of C_2, CN, OH, H_2O, CO, and CO_2.

The present investigation was undertaken to observe the effects of adding other fuels to the oxyacetylene flame and to observe the changes in intensity of the emission bands when the flame is irradiated with high-frequency discharges. Also the region from 3.7 to 4.1 μ was measured under high resolution to ascertain if any bands of low intensity could be observed between the OH and H_2O lines.

2. Experimental Method

A grating with 10,000 lines/in. was used in the spectrometer which resolved lines separated by 0.07 cm^{-1} in the 3- to 4-μ region. A description of the instrument, the methods of measuring the wavelengths, and other details are given in a previous publication [5].

The spectrum was observed of an oxyacetylene flame from a mixture enriched in fuel to enhance the bands selected for study. The radiation from the flame was intensified on the spectrometer slit by using a system of mirrors [6].

[1] This work was supported in part by the Geophysics Research Directorate, Air Force Cambridge Research Center.

[2] Figures in brackets indicate the literature references at the end of this paper.

3. Experimental Results

The use of the 10,000 lines/in. grating in the second order produced almost twice the resolution that was obtained in the first order. An example of the high resolution obtained is shown in figure 1. A part of the emission spectrum of carbon monoxide is shown for the region from 4,250 to 4,310 cm^{-1}. The band head of the 3–1 band occurs at 4,306 cm^{-1} and the figure includes the lines of the R branch from R 13 to R 67. The lines from R 53 to R 67 are folded back over the region of the R lines extending from 33 to 48, but the two sets of lines are sufficiently resolved to be readily observed. When this band was measured with low resolution the lines from R 53 to R 67 were not observed [4]. Under the burning conditions when this spectrum was observed, the R 26 line of this band was the most intense. The lines from P 2 to R 12 of the 2–0 band also fall in this region. On account of the elevated temperature of the oxyacetylene flame the intensity of the rotational lines near the center of the 2–0 band is low. The first line of this band which stands out above the noise level is R 3.

Some bands observed in the infrared spectra of flames are weak in intensity, primarily on account of the low concentration of the molecules. By adding substances which increase the concentration of the molecule or radical under observation, the spectra can be made more intense. An example of such a change in intensity is the CN spectrum which was observed in the flame with and without added gases. It was found that the CN spectrum was greatly increased in intensity when N_2O was introduced into the fuel line. Two traces of the spectrum of CN are shown in figure 2. Because this band occurs in the near infrared region, higher resolution was obtained by using a 15,000 lines/in. grating in the second order. The upper curve was observed with a flame which was rich in fuel. The inner cone extended about 2 in. above the tip of the burner. A region near the top of the inner cone was focused on the entrance slit of the spectrometer. The lower trace was obtained under the same conditions of measurement, but a small amount of N_2O was added to the acetylene before burning. The N_2O produced an increase in intensity of about 50 percent in the lines of this band. By adding larger amounts of N_2O the intensity of the band was increased by a factor of

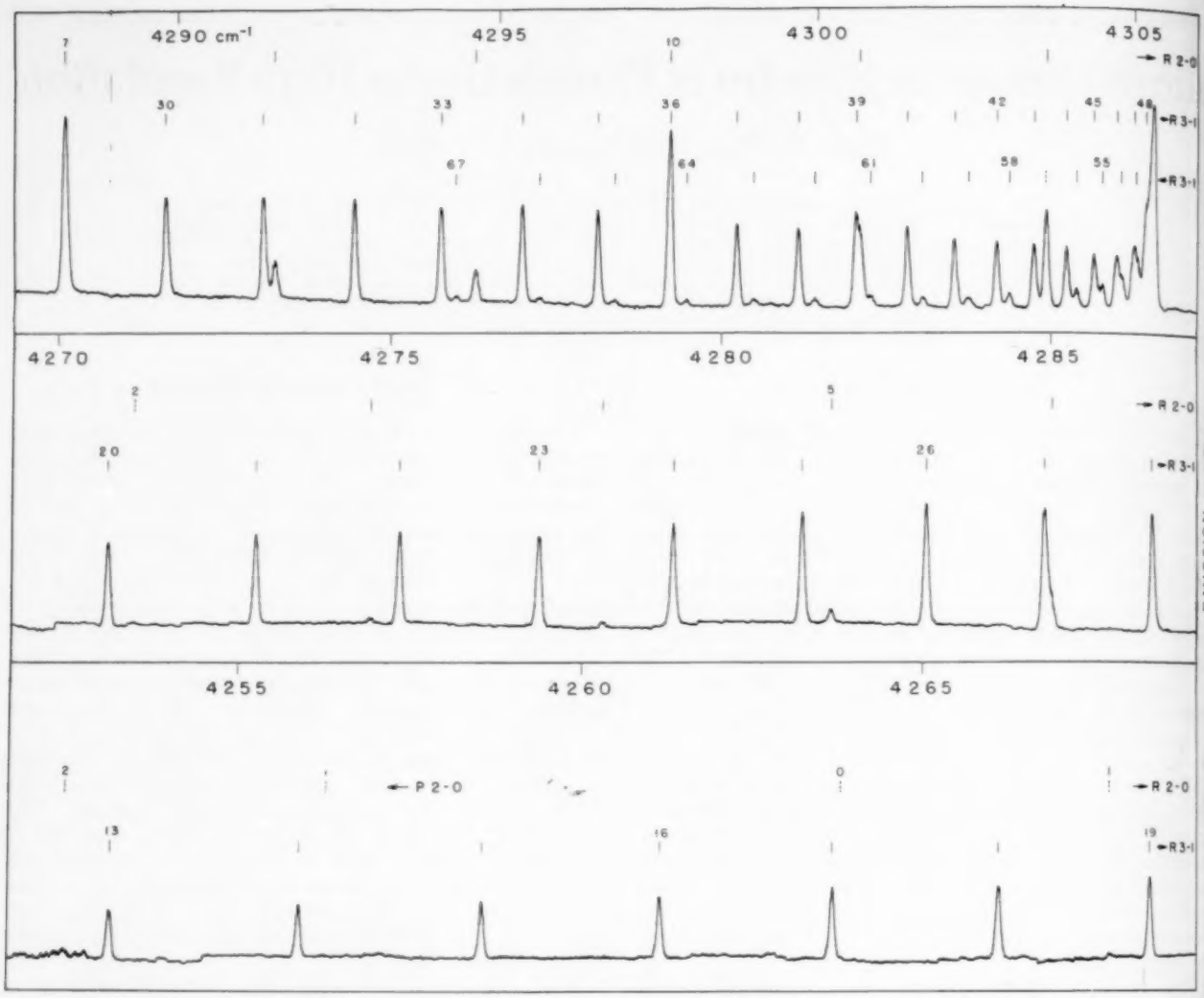

FIGURE 1. *The emission spectrum of* CO *for the 3–1 transition in the region from 4,250 to 4,310 cm*$^{-1}$.
Some of the lines of the 2-0 transition also occur in this region.

four. However, the flame was not stable and the entire band could not be observed under the same conditions.

The infrared emission of gases excited by a radio-frequency discharge has been reported by Wilkinson, Ford, and Price [7]. They found that the spectrum contained many bands which arose from transitions of the high energy levels of the molecules, and for CO the transitions from 2–0 and 12–10 were observed. On the other hand, in the oxyacetylene flame only the transitions from 2–0 to 8–6 are present with appreciable intensity. The emission spectra from the oxyacetylene flame should be increased in intensity when excited by a radiofrequency discharge. The results obtained with such a discharge through the flame are shown in figure 3. The upper curve is the 2–0, 3–1, and 4–2 transitions of the CO spectrum observed with a rapid scanning rate. The lower curve is the spectrum of the same region with the radiofrequency discharge passing through the flame. Although the high-frequency machine was of low output (100 w) a considerable change in the intensity of the rotational lines can be observed. All the lines of the spectrum observed with the high-frequency discharge have been increased in intensity, and the intensity ratio of the higher transitions to lower transitions has been increased. The intensities of the lines of oxyacetylene flame in the 3–1 and 2–0 bands are about equal, but with the discharge through the flame the 3–1 band is about 50 percent more intense. These preliminary results indicate that the use of the high-frequency discharge in the flame should be of importance in the observation of flame spectra.

The emission spectra of oxyacetylene flames in the region from 3.0 to 3.5 μ are rich in lines which belong to the bands of water vapor. When the spectrum is extended to longer wavelengths the P branch of the OH band is the most characteristic feature observed. Between the OH lines there are weak lines which cannot be resolved with medium resolution. The region from 3.5 to 4.0 μ has now been remeasured

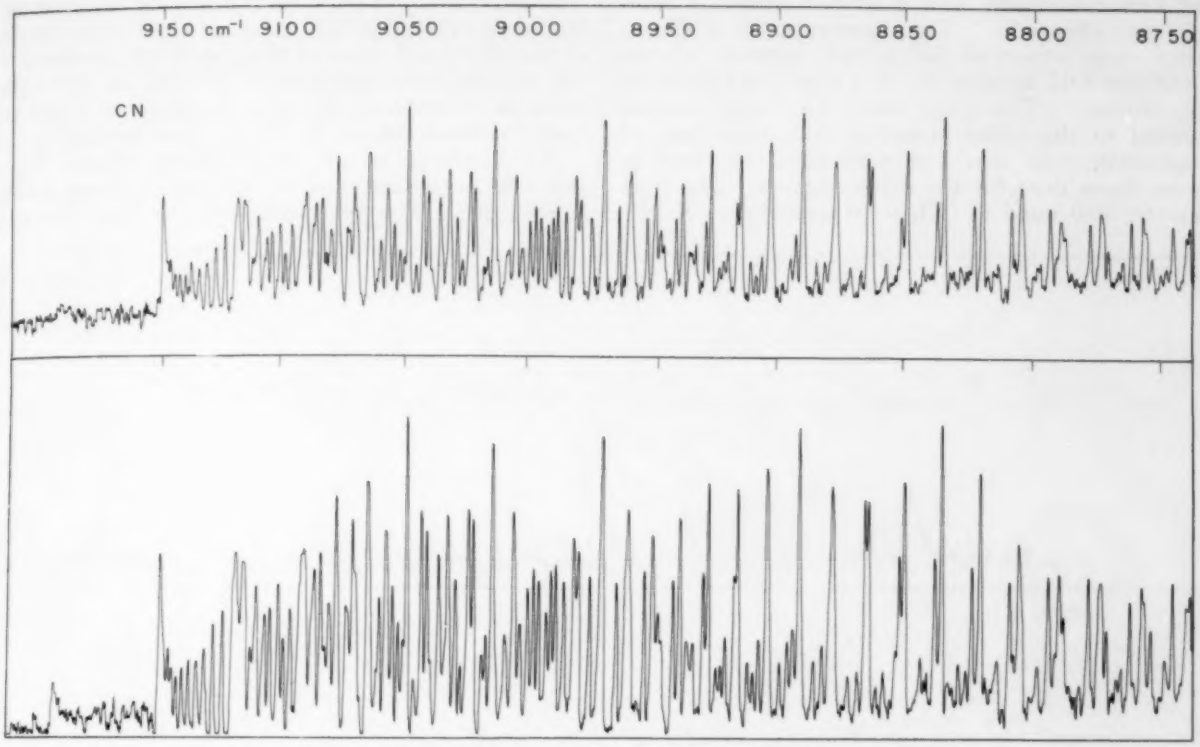

FIGURE 2. *The spectrum of* CN *from 8,750 to 9,150 cm*$^{-1}$.
The lower curve is the spectrum obtained when N_2O has been added to the fuel.

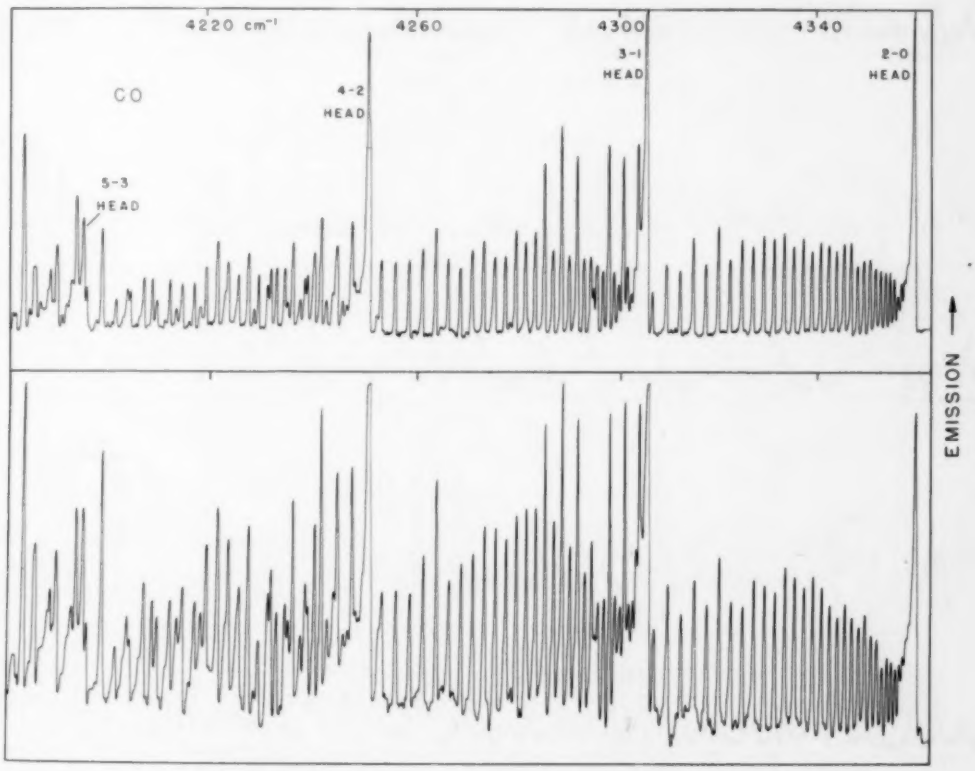

FIGURE 3. *The emission spectrum of* CO *in the first overtone region.*
The lower curve was obtained when the flame was irradiated with a high-frequency discharge.

under high resolution, and a large number of lines have been observed. The spectrum of a flame, figure 4, was observed for a rich mixture of the fuel and the OH lines of the 2–1 and 1–0 bands are fairly intense. The CO_2 band was very intense compared to the other structure and that part of the spectrum was observed with slits one-third as large as those used for the other regions. The lines of the 001–000 band of CO_2 were resolved to R 118. The band head of 01′1–01′0 is double on account of the l-type doubling and some of the l-type doublets of the R-branch lines of this band are resolved, but the atmospheric absorption of CO_2 in the optical path of instrument becomes so large at 2,380 cm^{-1} that the band cannot be observed to its center.

The spectrum of a hydrogen-oxygen flame (fig. 5) has also been observed for the region from 2,370 to 2,660 cm^{-1}. The spectrometer slits were two-thirds

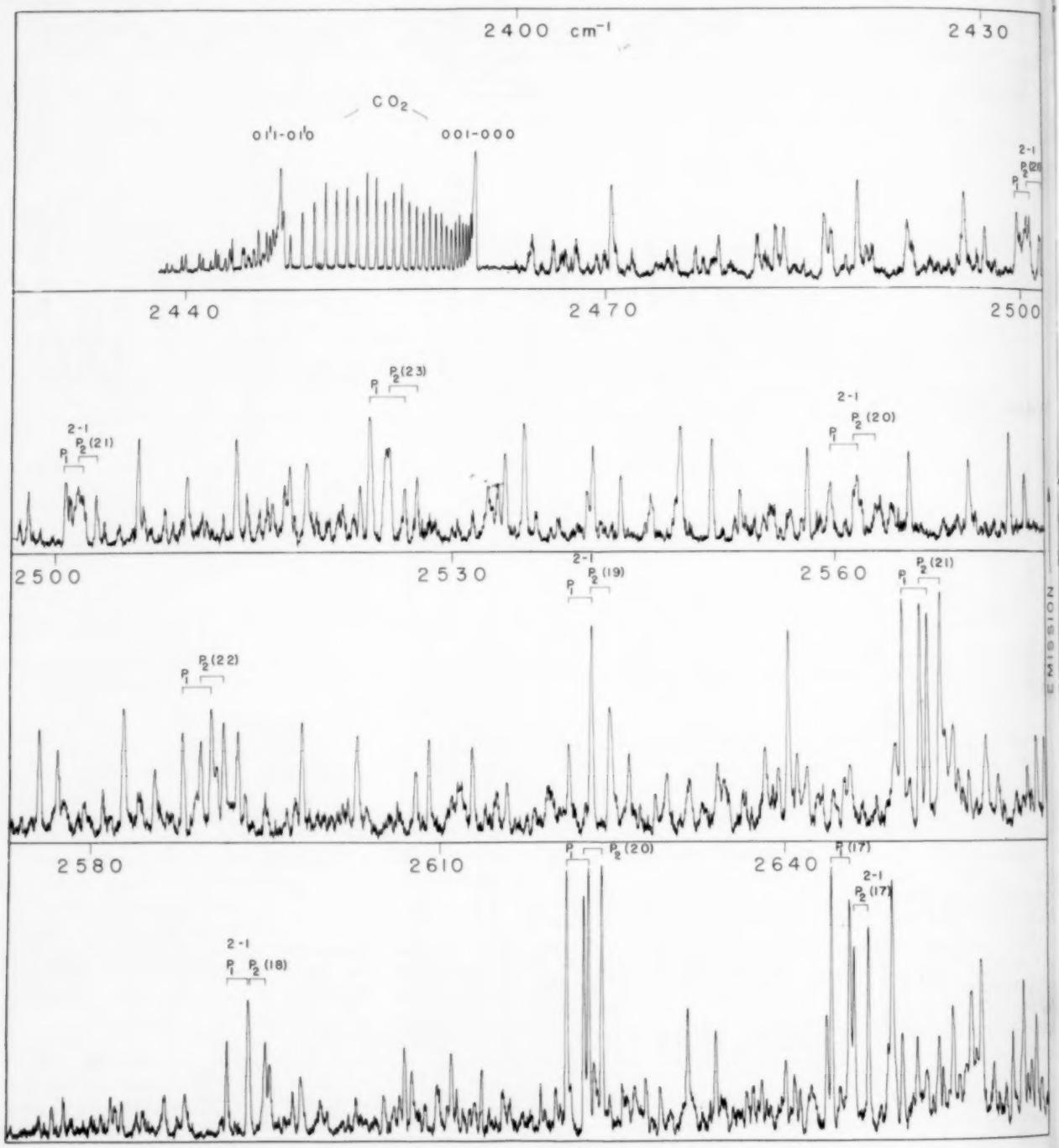

FIGURE 4. *The emission spectrum of an oxyacetylene flame from 3.7 to 4.1 μ.*

Part of the CO_2 spectrum and some of the lines of OH are a prominent part of the spectrum.

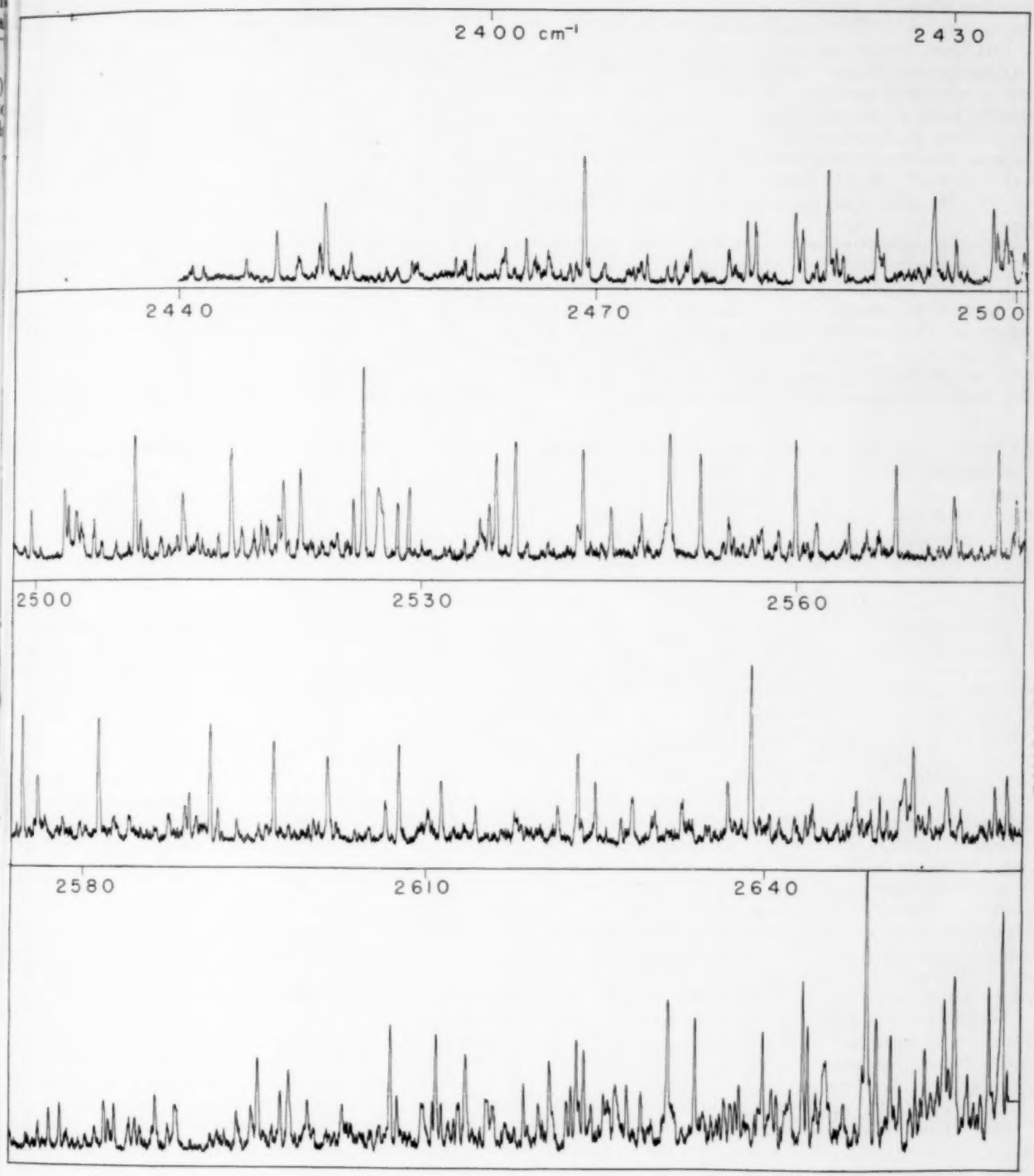

FIGURE 5. *The emission spectrum of a hydrogen-oxygen flame from 3.7 to 4.1 μ.*
Many of the lines in this spectrum correspond with those observed in the oxyacetylene spectrum.

as wide for measurements of figure 5 as for those of figure 4, but all other operating conditions of the instrument were the same.

The spectrum of the hydrogen-oxygen flame contains OH lines which are less intense than those in the oxyacetylene flame. Also, the CO_2 bands are absent in the hydrogen-oxygen flame. Most of the remaining lines of the spectrum are more intense in figure 5 than in figure 4. The region from 3.0 to 3.7 μ was also measured and many lines were observed. Almost all of these lines arise from the bands of OH and the $2\nu_2$ and ν_3 bands of water vapor.

The identifications of most of the lines in the 3.7- to 4.1-μ region, other than those of OH and CO_2, have not been made. A few lines fall in the series which have been identified as a part of ν_3 rotational structure of H_2O. The remaining lines may be a part of the ν_2 or ν_3 band of water vapor, but at present it has not been possible to identify them as arising from the transitions in those bands.

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WASHINGTON, May 23, 1958.

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Improved Description of Hafnium Spectra

Charles H. Corliss and William F. Meggers

Earlier descriptions of atomic hafnium spectra, from conventional arcs or sparks, have been handicapped by the absence of pure samples and by the presence of a strong background of molecular spectra. Recent availability of highly purified hafnium metal, and the development of a new light source, removed these handicaps. This improved description of hafnium spectra was made by employing electrodeless metal-halide lamps excited, at relatively low pressure and temperature, by microwaves. Lamps of hafnium iodide, hafnium bromide, and hafnium chloride were compared to recognize the spectra of halogens or their compounds and thus arrive at the atomic hafnium lines common to different lamps. The number of lines now ascribed to hafnium spectra exceeds 6,200 as compared with about 2,400 heretofore. The wavelengths range from 1284.88 to 12043.08 A, and estimated relative intensities in different light sources (including arcs, sparks, and electrodeless lamps) indicate which lines belong to Hf I, Hf II, Hf III, and Hf IV. The splitting of spectral lines in magnetic fields (Zeeman effect) has also been improved by using magnetic fields of higher intensity, and greater spectrographic resolving power than before. The number of lines for which Zeeman patterns have been observed has been increased from 280 to 1,030, and the types of complex patterns invariably confirm the assignments of lines to Hf I or Hf II.

Hafnium was the next to the last stable element to be discovered in the earth's crust; its discovery was announced by Coster and Von Hevesy [1][1] in a letter to Nature on January 20, 1923. That year Hansen and Werner [2] published the first description of the optical spectra of hafnium, consisting of wavelengths of 807 lines ranging from 2253.98 to 7240.9 A, and estimated relative intensities in arc and spark spectra.

In 1925 Professors Bohr and von Hevesy generously presented about 0.2 gram of their purest hafnium to Meggers [3] who made another description of hafnium arc and spark spectra for the purpose of finding regularities among the lines. Spectrograms were made by burning small portions of the sample in a silver arc or spark, and wavelengths from 2155.72 to 9250.27 A were measured for some 2,100 spectral lines. However, careful comparison with known spectra proved that 609 of the observed lines were due to impurities, among which niobium, zirconium, and titanium were the most abundant. Nevertheless this list of about 1,500 hafnium lines, because of its effective separation of Hf I and Hf II spectra by comparing arc and spark intensities, permitted the detection of regularities in both spectra.

In 1928 Meggers and Scribner reported [4] the first multiplets in Hf II, and in 1930 they published [5] the first regularities in Hf I. It was recognized that extension and confirmation of these first regularities would require further improvements in the basic descriptions of hafnium spectra and also observation of the Zeeman effect. Both requirements were partially met in 1932 when hafnium spectra were reobserved with purified oxide donated by Prof. von Hevesy, and the first Zeeman-effect spectrograms were made with a small rod of hafnium metal presented for this purpose by Dr. G. Holst of Eindhoven. The arc and spark spectra were remeasured, and extended from 1990.73 to 10637.92 A. The new sample of hafnium oxide was entirely free from titanium and showed only a trace of niobium, but it contained considerable amounts of zirconium and nickel. The number of spectral lines positively identified with hafnium atoms or ions was increased from about 1,500 to 2,400, including nearly 1,400 Hf I, about 1,000 Hf II, and several dozen Hf III lines. Magnetic splitting (Zeeman effect) was observed for 280 hafnium lines (2393 to 4817 A), 70 belonging to the first and 210 to the second spectrum. These confirmed the first reported [4, 5] regularities in the spectra, and full details of the new wavelengths, intensities, Zeeman data, and quantum interpretation of the second spectrum of hafnium were published by Meggers and Scribner [6] who promised that "Further data and analysis of the Hf I spectrum will be published after they have been supplemented by additional observations of Zeeman effects, since the data at present available have proved insufficient for the complete identification of Hf I spectral terms"

Further progress in the investigation and interpretation of the Hf I spectrum was delayed many years for the following reasons: it was proved that the Zeeman data were inadequate, many impurity lines were always present, and it was suspected that the line list was far from complete. In his 1928 paper on wavelength measurements in spectra of hafnium Meggers stated [2] "The greatest difficulty in describing the arc spectrum of hafnium arises from the band spectrum which probably originates with the oxides. Some of these bands are very strong and extremely complex over long spectral ranges. In many cases it is impossible to decide if faint lines belong to Hf I or to the HfO_2 spectrum". Attempts to improve the description of the hafnium arc spectrum with electrodes of solid hafnium metal kindly donated in 1951 by C. P. Keim of the Oak Ridge National Laboratory were frustrated by the strong background of HfO spectra from 3000 A to the infrared limit of photography, and by the presence of metallic impurities, mostly zirconium.

Before hafnium was discovered, the accepted

[1] Figures in brackets indicate the literature references on page 272.

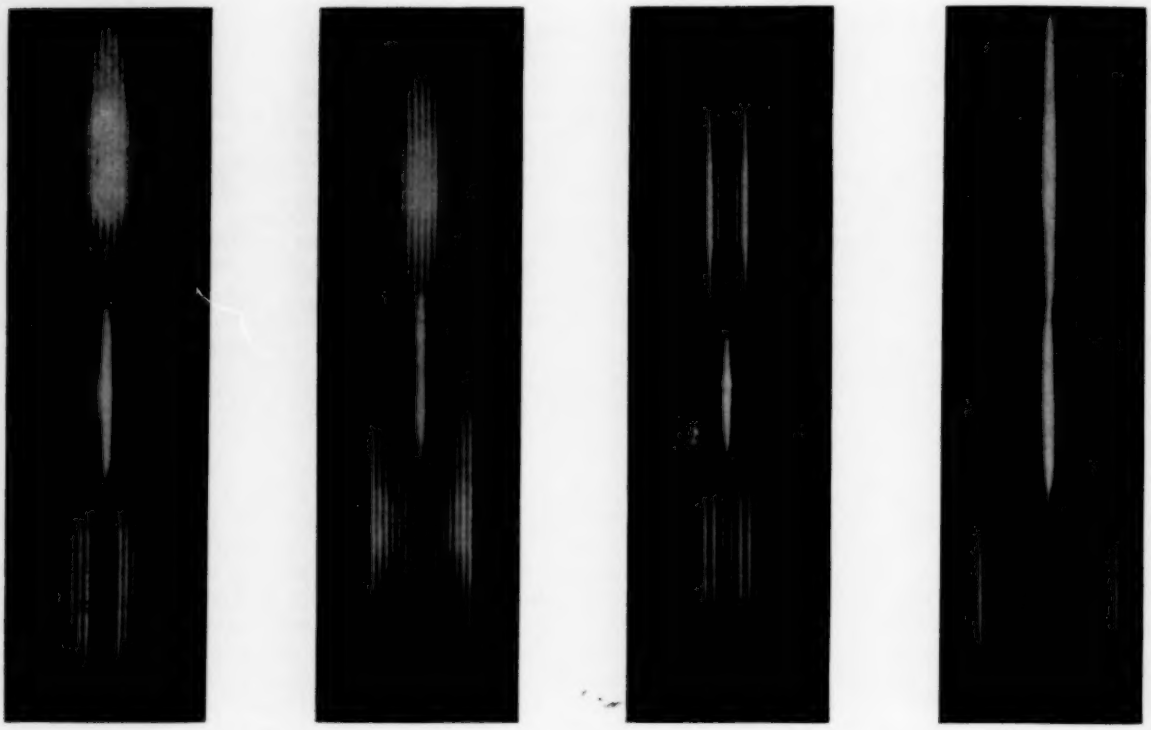

FIGURE 1. *Types of Zeeman patterns for* Hf I *observed at NBS using electrodeless lamps in a field of 37,000 oersteds.*

chemical atomic weight of zirconium [7] was more than a half-unit larger than its present value, 91.22. This difference was later explained [8] by the unsuspected presence of hafnium as an impurity in the earlier samples of zirconium. Likewise, after information about the spectra of hafnium became available it was found [3] that all earlier descriptions of zirconium spectra contained many hafnium lines. The complete separation of hafnium and zirconium is one of the most difficult chemical operations, and to this day neither has been obtained spectroscopically free from the other. However, since certain properties of these metals have recently been found to be useful in the construction and operation of nuclear reactors, greater efforts have been made to provide large quantities of high-purity hafnium and zirconium.

In December, 1955, two rods of hafnium metal, ¼-in. diameter, 4-in. length, were generously provided for our further spectroscopic investigations by Stephen M. Shelton of the U. S. Department of Interior, Bureau of Mines. A complete quantitative spectrochemical analysis of these samples was also provided; it expressed the impurities in parts per million as follows: Cd <0.5, B 0.2, Al 20, Fe 500, Cu 40, Pb <10, Cr <30, Si 150, Mg 40, Ti 100, Zn <50, Ni 40, Mn <10, Mo 60, V 40, Co <5, Sn $<$ Zr 80. Thus the total impurities of these samples approximate 0.1 percent, and zirconium, which was always the most troublesome, constitutes only 0.008 percent. Of these impurities, only the stronger lines of Fe, Si, Ti, Zr, Zn, and Al were observed in the electrodeless lamps described below.

Recently, a new type of light source was described by Corliss, Bozman, and Westfall [9], who showed that a bright emission spectrum of any metal could be obtained from out-gassed quartz tubes inclosing a minute amount of any volatile compound of that metal, when excited by microwaves. The first hafnium lamp of this type was made by producing, in an evacuated quartz tube, a chemical reaction between filings of the above-mentioned hafnium metal and a small crystal of iodine. The spectrum emitted by this lamp was photographed from 2000 to 12000 Å; it was much richer than any hafnium arc spectrum because it completely suppressed the usual HfO bands that always obscured several thousand hafnium lines of low or moderate intensity. The only defect was the presence of some strong iodine lines and an entirely new system of bands, presum-

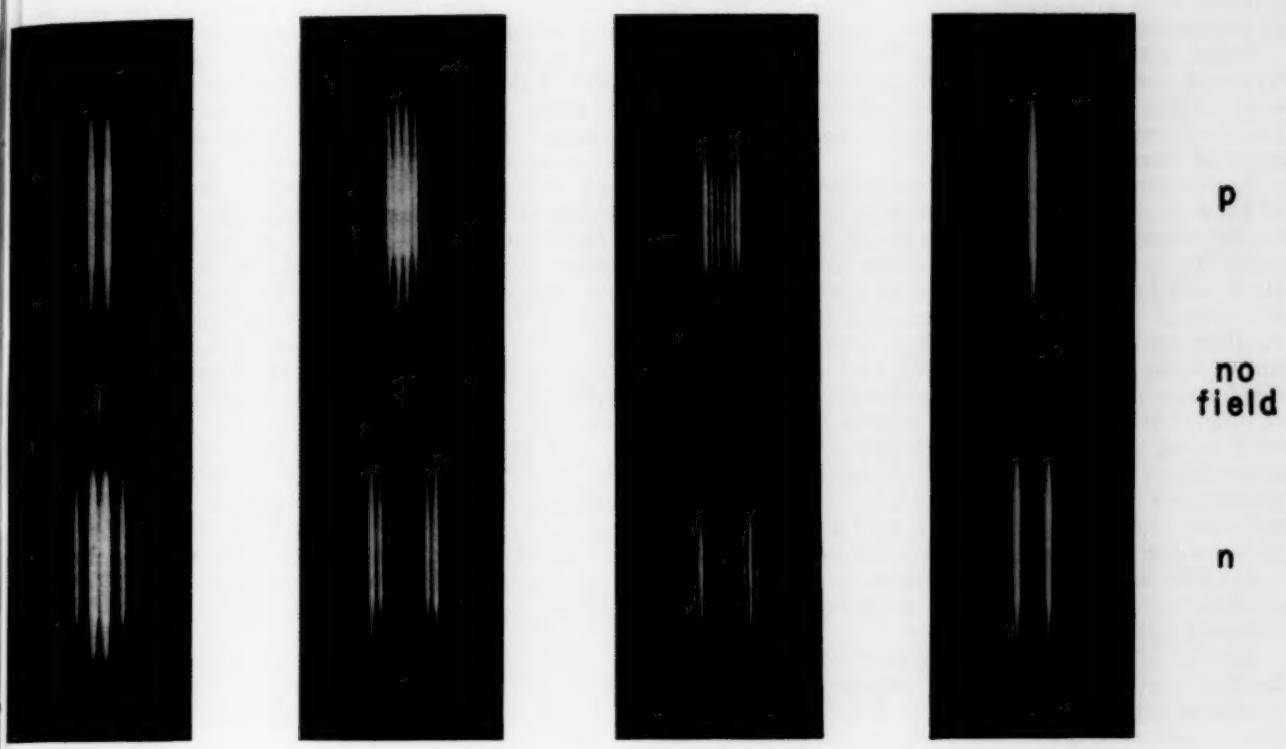

FIGURE 2. *Types of Zeeman patterns for* Hf II *observed at NBS using electrodeless lamps in a field of 37,000 oersteds.*

ably due to hafnium iodide which appeared with low intensity in several short intervals of spectra. These lines and bands were replaced by others when the lamps were made either with hafnium bromide or with hafnium chloride. Thus by observing and comparing the spectra of two different halides the halogen lines and molecular bands are completely recognized as differences whereas the atomic spectra of hafnium (and its impurities) are mutually confirmed. Such a comparison between hafnium iodide and hafnium bromide spectra was made between 2000 and 6500 A, but, because many very intense bromine lines appear in the red and near infrared, a lamp containing hafnium chloride was used in these regions to confirm hafnium spectra emitted by the hafnium iodide lamp. Among the three hafnium halides, hafnium iodide was the easiest to prepare and its hafnium spectra were more intense and less blended with halogen lines because iodine emits no strong lines between 2062 and 4100 A.

These lamps were excited with a commercial diathermy unit of 125 w power and 2,450 mc frequency, and were observed end on. The spectra above 2000 A were dispersed by 22 ft radius concave diffraction gratings in Wadsworth stigmatic mountings. Two 6-in. gratings were used, one ruled 15,000 and the other 30,000 lines per inch. The spectrographs and photographic plates employed in recording hafnium spectra have been described [10] in a paper on the spectra of rhenium. When the hafnium spectrograms were made no effective way of varying the excitation of the metal halide lamps was available to distinguish Hf I from Hf II lines. Therefore, on each spectrogram a series of exposures was made of successive increments of slit illuminated by the d-c arc in air, the high-voltage condensed spark in air, the spectrum of the hafnium halide lamp, and the arc spectrum of iron. The last provided international standards of wavelength for measurements of hafnium lines by interpolation and the others permitted the assignment of all hafnium lines to the proper atom or ion. It was observed that the hafnium halide lamp emitted Hf I lines with the greatest intensity, sharpness, and number, but it also gave with lower intensity but equal sharpness practically all of the Hf II lines, which usually appear as broad, hazy, or unsymmetrical lines in the spark. Because the metal

halide lamps operate at a much lower pressure and temperature than the conventional arcs and sparks they emit sharper lines, and one should apologize for measuring their wavelengths relative to the international standards obtained from an iron arc at atmospheric pressure.

Below 2000 A a normal incidence vacuum spectrograph containing a 2-m radius glass grating ruled with 30,000 lines per inch was used to photograph hafnium vacuum arc and spark spectra with reciprocal dispersion of 4.2 A/mm.

In addition to wavelengths and relative intensities of lines in different light sources, it is desirable, for an improved description of hafnium spectra, to observe the Zeeman effect on as many lines as possible. Back and Landé [11] have shown that only 6 types of resolved Zeeman patterns exist, 3 for even multiplicities and 3 for odd. A 7th type has a single undisplaced p component and two symmetrically displaced n components; it is generally characteristic of singlet terms or other transitions between levels with equal g values. These 7 types have all been observed in hafnium spectra; typical patterns are reproduced in figures 1 and 2 where types 1, 2, 3 are uniquely characteristic of Hf I, and 4, 5, 6 of Hf II. This sorting of Hf I and Hf II on the basis of Zeeman types was in perfect agreement with the separation of these spectra according to relative intensities in different light sources.

Besides of great value for sorting spectra, resolved Zeeman patterns are almost indispensable for the quantum interpretation because the quantum numbers (j) associated with the total angular momentum of the radiating atom are given directly by the number of components, and the intervals between neighboring components equal the difference between the magnetic splitting factors (g) of the combining levels. The first observations of Zeeman-effect in hafnium spectra have already been mentioned [6]; they greatly facilitated the analysis of Hf II, but were inadequate for an extensive analysis of Hf I because they were made with a spark operated in a 6-mm pole gap of a Weiss magnet producing a field intensity of 35,000 oersteds. In August 1949 greatly improved Zeeman spectrograms were obtained by courtesy of G. R. Harrison of the Massachusetts Institute of Technology, by using an arc in a magnetic field of 83,000 oersteds produced by the Bitter magnet [12]. The gratings available at MIT also had 2 or 3 times the resolving power of the one employed at the Bureau, but the MIT gratings had very low efficiency for waves longer than about 5000 A. The MIT Zeeman spectrograms of hafnium were therefore supplemented from 5000 to 9000 A by recent observations at the Bureau with a hafnium-iodide lamp in a magnetic field of 37,000 oersteds. The patterns reproduced in figures 1 and 2 were taken from these spectrograms.

The results of the final effort to provide an improved description of hafnium spectra are presented in table 1, where measured wavelengths, estimated relative intensities in arc, spark, and tube spectra, assignment of individual lines to successive spectra, and Zeeman types are shown in successive columns. Notation in the table conforms to the report of Subcommittee e of the Joint Commission for Spectroscopy [13]. Further details of the Zeeman effect are reserved for reports on the quantum interpretation of Hf I and Hf II; in the present paper the Zeeman-type numbers suffice to confirm the assignment of particular lines to their proper spectrum as inferred from relative intensities in different light sources.

The generous donations by C. P. Keim and by S. M. Shelton of massive metallic electrodes of hafnium for our investigations of hafnium spectra are gratefully acknowledged by the authors. Also we thank G. R. Harrison for letting us use the excellent equipment at MIT for observing the Zeeman effect.

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TABLE 1. *Emission spectra of hafnium*

Wavelength in vacuum	Intensity		Spectrum	Wavelength in vacuum	Intensity		Spectrum
	Arc	Spark			Arc	Spark	
A				*A*			
1284.88		1		1628.90	8	18	II
1305.24		15e	IV	1630.07		3	
1337.08		3		1630.83	5	15	II
1357.40		12e	IV	1631.58		1	IV
1366.34		3		1633.64		2	IV
1386.69		5	III	1633.82		1	IV
1390.39		40	IV	1634.70		1	IV
1396.66		3	IV	1638.51		1	IV
1400.12		1	IV	1638.66		1h	IV
1407.18		2	IV	1640.41		4h	IV
1408.39		2	IV	1641.38		1	
1412.23		1	IV	1641.91		5	
1413.53		2	IV	1642.36		2	
1433.44		2	IV	1644.22		4	
1437.29		4	IV	1647.40		1	IV
1437.76		8e	IV	1649.87	1	2	II
1445.42		4	IV	1652.75	1	10	III
1449.83	3	20	III	1658.59		1	IV
1457.17		1		1659.65		1	
1457.95		3	IV	1660.64		4	IV
1462.81		4		1661.64		1	IV
1487.50		4		1662.55		4	III
1491.67	1	50e	IV	1663.29		1	
1495.73		1	II	1664.77		4	
1497.42		1		1666.86		1	IV
1507.82	15e	30	III	1667.85		1	
1508.52		1		1672.58		1	IV
1520.13		2		1673.38	5	5	II
1526.63		1		1674.37	10	10	II
1528.82		35e	IV	1679.62	6	8	II
1530.51	1	12	III	1683.95	20	50	III
1541.26		1		1691.18		1	II
1542.04	3	10	II	1692.53		2	
1546.45	2	3	II	1693.34	7	18	III
1548.19		12	IV	1698.01		1	IV
1550.78		8	IV	1698.50		1	IV
1555.68	1	3	II	1700.19	1	12	III
1557.00		1	IV	1711.86		6	
1560.18		15e	IV	1716.24	7	10	II
1561.07		2		1717.21	2	100	IV
1567.27	8	10	II	1718.57		20	IV
1572.03		25e	IV	1719.33		1	IV
1577.07		5		1720.12	1	5	III
1585.99		1		1720.32	2	10	III
1592.99	5	8	II	1722.70	1	8	III
1593.45		2		1728.03	3	3	II
1596.54		5	III	1729.11		3	IV
1601.02		6	III	1731.84		4	IV
1603.98		2	IV	1733.90		2	II
1604.49		1	IV	1733.97		6	IV
1606.70		12	III	1735.16	1	15	III
1614.17	2	3	II	1738.32	1	10	III
1617.80		1	IV	1738.74	1	6	III
1618.27		4		1739.60	1	8	III
1619.31		1h		1741.75		2	IV
1621.32		1h		1746.80		5	III
1623.03	6	15	II	1747.17	4	10	III
1626.76		1		1749.12		10e	IV
1627.61		1		1750.20		10e	IV
1628.04		1		1756.91	25e	50	III

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TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in vacuum	Intensity		Spectrum	Wavelength in vacuum	Intensity		Spectrum
	Arc	Spark			Arc	Spark	
A				*A*			
1759.87	----	1		1875.81	----	6	III
1760.92	----	3	IV	1877.74	6	15	III
1761.27	----	1	IV	1879.26	1	1	II
1764.63	1	2	III	1879.77	----	1	
1764.90	----	3		1883.34	----	5	III
1765.23	----	3		1885.15	50	150	III
1765.64	----	2	IV	1885.21	1	3	III
1770.22	----	4	III	1888.21	8	20	III
1772.63	1	2	II	1888.90	2	10	III
1774.05	----	1		1889.42	30	80	III
1774.47	----	1		1892.30	----	1	II
1774.76	20	12	II	1893.86	----	1	
1775.36	1	2		1897.49	3	4	II
1779.60	----	1		1900.85	18	25	III
1782.66	----	1	IV	1901.39	8	8	II
1783.27	----	1	IV	1903.10	----	1	
1784.40	----	2		1904.26	2	12	III
1784.58	----	3		1905.61	10	15	III
1785.22	25	25	III	1909.18	----	3	
1786.96	----	4	III	1909.45	2	4	II
1788.35	----	6h	III	1910.21	----	4	
1790.09	----	1	II	1912.99	1	10	III
1791.48	----	1		1913.47	----	2	
1792.27	----	7	III	1916.69	25	60	III
1793.17	3	8	II	1917.73	3	----	I
1793.43	1	10	III	1919.52	15	30	II
1793.84	----	1	IV	1922.13	12	15	II
1797.01	20	20	III	1922.74	20	25	II
1801.28	----	2		1927.52	----	1	
1805.66	----	4	III	1928.12	12	30	III
1813.64	2	15	III	1929.78	----	1	IV
1815.65	10	18	II	1931.65	20	40	III
1815.98	3	4	II	1934.00	1	12	III
1816.20	4	5	II	1935.50	----	1	
1819.56	----	4h	IV	1936.39	----	2	II
1823.63	----	2	IV	1937.80	----	7	III
1825.31	3	5	II	1937.92	1	1	II
1826.03	20	35	III	1938.33	1	8	III
1828.36	----	1	II	1939.65	----	1	
1832.97	----	2		1941.98	----	1	
1835.52	----	1		1942.27	2	----	I
1838.79	3	18	III	1942.74	----	1	
1839.50	----	2		1943.41	----	1	
1841.51	----	1		1944.32	3	3	II
1843.64	40	60	III	1944.91	----	1	II
1847.77	----	3		1947.03	----	1	
1848.47	----	1		1949.32	1	6	III
1849.19	----	2		1950.81	2	8	III
1850.64	1	----	I	1952.04	----	1	IV
1852.50	----	3		1952.37	----	1	
1853.97	2	9	III	1952.77	4	20	III
1854.23	----	4		1955.68	12	18	II
1856.33	5	40	III	1959.73	3	3	II
1863.04	1	5	III	1959.89	----	1	II
1869.37	10	10	II	1961.24	----	1	
1870.58	30	60	III	1962.49	4	3	II
1871.70	----	5	III	1963.06	8e	50	III
1873.54	----	1		1963.82	12	5	II
1873.71	2	1	II	1964.26	20	15	II
1874.81	20	50	III	1966.59	----	1	

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in vacuum	Intensity		Spectrum	Wavelength in vacuum	Intensity		Spectrum
	Arc	Spark			Arc	Spark	
A				*A*			
1972. 81	------	1	----------	1988. 22	1	6	III
1974. 01	35	50	III	1989. 00	5	------	I
1974. 21	18	25	III	1989. 61	2	10	III
1976. 19	------	1	IV				
1977. 61	2	------	I	1991. 44	100	100	III
				1993. 01	------	1	II
1979. 19	2d	------	I	1993. 15	5	4	II
1979. 72	------	1	----------	1993. 58	1	1	----------
1980. 63	12	8	II	1993. 82	10	8	II
1982. 44	10	7	II				
1983. 24	3	------	I	1996. 61	1	1	II
				1998. 04	40	40	III
1983. 75	------	3	III	1999. 21	------	1	----------
1986. 38	1	------	I				

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
2000. 62	------	4	----------	------	2041. 78	1	2	----------	------
2001. 78	------	1	----------	------	2042. 14	3	------	I	------
2002. 06	40	40	III	------	2043. 87	3	12	III	------
2002. 72	1	4	III	------	2044. 96	1	3	----------	------
2003. 03	------	1	----------	------	2047. 56	6	10	II	------
2005. 37	3	3	II	------	2047. 84	1	------	I	------
2006. 53	------	1	IV	------	2051. 70	1	10h	III	------
2007. 64	1	2	III	------	2053. 14	------	3	----------	------
2007. 77	------	2	II	------	2053. 54	2	------	I	------
2011. 96	------	1	II	------	2054. 46	4	100	IV	------
2012. 78	30	15	II	------	2054. 87	2	1	II	------
2013. 37	12	8	II	------	2055. 30	2	------	I	------
2014. 06	------	7	IV	------	2055. 35	------	4h	II	------
2015. 69	10	8	II	------	2056. 16	1	------	I	------
2016. 30	2	3	II	------	2057. 40	1	3	II	------
2017. 21	1	1	II	------	2058. 56	------	1	II	------
2017. 90	1	------	I	------	2060. 48	4	9h	II	------
2018. 81	------	2	----------	------	2061. 48	4	8	II	------
2020. 07	15	10	II	------	2063. 24	1	2	II	------
2022. 13	4e	20	III	------	2064. 46	1	2	II	------
2022. 59	2	------	I	------	2064. 79	10	12	II	------
2024. 08	------	1	----------	------	2065. 55	------	2h	II	------
2024. 62	------	1	----------	------	2065. 72	1	------	I	------
2025. 02	------	1	II	------	2066. 20	1	2h	II	------
2025. 37	7	10	II	------	2068. 59	3	5	----------	------
2025. 50	------	1	II	------	2068. 84	10	10H	II	------
2028. 18	30	25	II	------	2070. 94	------	300	III	------
2029. 03	1h	2h	II	------	2071. 48	3	------	I	------
2029. 89	10	18	II	------	2072. 87	2	------	I	------
2031. 68	1	1	II	------	2075. 95	3	------	I	------
2035. 93	------	3	IV	------	2076. 10	------	4H	II	------
2036. 25	9	8	II	------	2076. 48	2	------	I	------
2037. 32	1	1	II	------	2076. 72	1	3h	II	------
2037. 76	60	100	III	------	2079. 12	1	1	II	------
2039. 09	15	15	II	------	2079. 72	1	1	II	------

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
2082. 80	5	6	II		2132. 28	1	3	II	
2083. 80	7	20	II		2133. 36	1	2H	II	
2084. 59	2	------	I		2134. 53	3	15	II	
2085. 19	2	------	I		2135. 65	2	------	I	
2085. 33	------	150h	III		2136. 48	------	20h	III	
2086. 30	3	5h	II		2137. 20	2	3	II	
2086. 80	1	2	II		2137. 54	1	------	I	
2087. 43	3	------	I		2138. 57	3	------	I	
2087. 67	3	------	I		2139. 22	7	30	II	
2087. 71	------	2h	----------		2139. 86	1	------	I	
2088. 77	10	30	II		2139. 93	------	5H	III	
2089. 39	1	------	I		2141. 82	4	10	II	
2089. 56	2	------	I		2142. 36	5	------	I	
2089. 95	4	15	II		2144. 16	2	5h	II	
2090. 83	8	20	II		2144. 71	1	------	I	
2093. 22	2	------	I		2146. 97	------	10	III	
2093. 27	------	3h	----------		2149. 83	3	------	I	
2094. 33	1	2h	II		2149. 94	------	5H	III	
2094. 54	3	------	I		2150. 06	2	2	II	
2096. 18	20	100	II		2150. 17	2	------	I	
2097. 35	------	3H	III		2150. 27	3	------	I	
2099. 30	------	200h	III		2150. 34	------	8hl	II	
2100. 59	1	------	I		2151. 67	5	------	I	
2102. 80	------	50	III		2152. 65	------	20h	III	
2104. 92	------	40	III		2153. 54	2	------	I	
2105. 20	2	------	I		2154. 21	3	------	I	
2106. 20	------	40h	III		2154. 66	2	4h	II	
2106. 25	4	------	I		2155. 66	------	200	III	
2107. 47	7	20	II		2156. 42	10	20	II	
2108. 25	3	------	I		2158. 10	4	------	I	
2108. 56	2	------	I		2158. 16	------	10H	III	
2108. 61	------	4H	III		2159. 57	2	------	I	
2108. 98	3	------	I		2160. 46	------	2H	----------	
2110. 31	------	200h	III		2161. 57	4	------	I	
2110. 42	5	10	II		2161. 62	------	10H	III	
2111. 24	1	------	I		2162. 462	6	10	II	
2111. 47	1	------	I		2162. 95	3	------	I	
2111. 84	1	------	I		2163. 48	------	20	III	
2113. 14	3d	------	I		2164. 06	4	------	I	
2113. 92	2	5H	II		2164. 65	------	10h	III	
2115. 02	5	10	II		2165. 20	4	------	I	
2116. 80	1	------	I		2168. 81	------	6H	III	
2117. 95	2	3h	II		2170. 214	5	20	II	
2118. 69	6	------	I		2171. 88	3	------	I	
2119. 12	------	40	----------		2171. 92	------	4h	II	
2119. 59	2	------	I		2172. 77	3	------	I	
2119. 69	------	100h	III		2172. 959	2	4	II	
2122. 81	3	------	I		2173. 422	5	10	II	
2122. 94	3	10h	II		2174. 327	------	80	III	
2123. 32	1	------	I		2175. 354	15	20	II	
2123. 68	5	25	II		2175. 76	2	------	I	
2124. 58	10	50	II		2176. 41	1	------	I	
2126. 61	1	6H	III		2177. 393	------	10	III	
2127. 50	1	------	I		2178. 511	------	20	III	
2128. 17	2	------	I		2178. 908	30	50	II	
2129. 09	8	70	II		2180. 23	------	3Hl	III	
2130. 08	2	------	I		2181. 95	2	4h	II	
2130. 12	------	4h	II		2182. 65	------	4h	III	
2130. 98	4	------	I		2182. 73	1	------	I	
2131. 88	------	7H	III		2183, 505	------	200	III	

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum			Zeeman type
	Tube	Spark				
A						
2184. 30	3	------	I			-----
2184. 35	------	10H		II		-----
2184. 97	2	4		II		-----
2186. 29	2	------	I			-----
2187. 43	2	------	I			-----
2187. 91	3	------	I			-----
2188. 428	3	------	I			-----
2188. 72	1	------	I			-----
2188. 87	4	10		II		-----
2190. 212	10	20		II		-----
2190. 388	------	30			III	-----
2191. 26	1	3h		II		-----
2191. 32	------	2h		II		-----
2191. 78	6	8		II		-----
2192. 31	2	3		II		-----
2193. 196	4	------	I			-----
2193. 84	2	------	I			-----
2194. 12	1	------	I			-----
2194. 968	10	------	I			-----
2195. 435	------	200			III	-----
2195. 52	3	------	I			-----
2196. 03	4	------	I			-----
2196. 404	5	7		II		-----
2199. 58	3	5h		II		-----
2199. 84	2	------	I			-----
2201. 67	1	3h		II		-----
2202. 18	2	------	I			-----
2202. 97	1	2h		II		-----
2203. 40	1	------	I			-----
2204. 17	4	------	I			-----
2204. 63	2	------	I			-----
2206. 09	6	------	I			-----
2206. 11	------	10H		II		-----
2210. 05	2	------	I			-----
2210. 84	2	2h		II		-----
2211. 32	2	------	I			-----
2211. 86	2	3		II		-----
2212. 45	7	20		II		-----
2213. 54	------	100			III	-----
2214. 675	2	------	I			-----
2214. 86	------	15			III	-----
2217. 67	1	2h		II		-----
2218. 36	1	7		II		-----
2218. 45	1	------	I			-----
2219. 45	1	------	I			-----
2219. 50	------	2h		II		-----
2219. 60	1	------	I			-----
2220. 48	2	------	I			-----
2220. 55	------	5hl			III	-----
2221. 59	1	------	I			-----
2221. 88	------	10h			III	-----
2223. 35	1	2		II		-----
2223. 94	1	------	I			-----
2224. 26	6	10H		II		-----
2224. 30	------	5		II		-----
2225. 352	5	6		II		-----
2228. 180	5	6		II		-----
2228. 45	3	3h		II		-----
2228. 772	3	5		II		-----
2230. 35	4	------	I			-----

Wavelength in air	Intensity		Spectrum			Zeeman type
	Tube	Spark				
A						
2231. 42	2	4h		II		-----
2234. 59	------	200			III	-----
2235. 13	2	------	I			-----
2235. 41	1	------	I			-----
2235. 461	------	10			III	-----
2235. 635	4	------	I			-----
2236. 35	2	3Hl		II		-----
2239. 85	2	3h		II		-----
2240. 20	1	------	I			-----
2241. 34	------	8h			III	-----
2243. 16	5	------	I			-----
2243. 19	------	15hl		II		-----
2244. 24	2	------	I			-----
2246. 29	1	------	I			-----
2246. 62	------	2h			III	-----
2248. 20	1	3h		II		-----
2248. 33	1	------	I			-----
2248. 95	3	------	I			-----
2249. 01	------	5H			III	-----
2249. 85	3	7H		II		-----
2251. 85	3	6		II		-----
2253. 995	30	80		II		-----
2255. 162	20	60		II		-----
2257. 894	4	10		II		-----
2258. 32	2	------	I			-----
2258. 685	5	15		II		-----
2260. 25	2	------	I			-----
2261. 54	2	------	I			-----
2262. 015	5	------	I			-----
2262. 20	1	------	I			-----
2263. 37	2	2h	I			-----
2264. 847	------	30h			III	-----
2266. 521	10	15		II		-----
2266. 832	20	40		II		-----
2267. 35	2	3h		II		-----
2267. 582	2	------	I			-----
2267. 91	2	------	I			-----
2268. 686	4	------	I			-----
2268. 92	1	------	I			-----
2269. 483	3	------	I			-----
2269. 86	4	------	I			-----
2269. 91	------	6hl			III	-----
2270. 69	2	4		II		-----
2271. 14	2	2h		II		-----
2271. 453	5	------	I			-----
2273. 147	20	40		II		-----
2273. 92	3	------	I			-----
2274. 18	1	------	I			-----
2274. 545	2	------	I			-----
2274. 64	4	15		II		-----
2275. 26	1	------	I			-----
2275. 483	6	------	I			-----
2276. 43	2	3h		II		-----
2277. 166	40	150		II		-----
2279. 195	4	------	I			-----
2280. 072	4	------	I			-----
2281. 683	5	------	I			-----
2281. 82	1	3h		II		-----
2282. 80	3	------	I			-----
2283. 089	5	------	I			-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum			Zeeman type
	Tube	Spark				
A						
2283. 555	------	40h		III		-----
2284. 60	10	20		II		-----
2285. 42	3	5h		II		-----
2288. 551	4	------	I			-----
2288. 630	2	3		II		-----
2289. 28	2	------	I			-----
2291. 06	2	------	I			-----
2291. 64	8	10		II		-----
2292. 34	1	2h		II		-----
2292. 77	2	3Hl	I			-----
2294. 88	1	------	I			-----
2296. 13	4	6h		II		-----
2297. 42	1	------	I			-----
2297. 71	2	------	I			-----
2298. 336	9	20		II		-----
2298. 57	1	------	I			-----
2298. 80	1	3		II		-----
2299. 190	5	------	I			-----
2302. 116	1	3h		II		-----
2303. 22	1	2h		II		-----
2304. 343	6	------	I			-----
2304. 51	------	1h		II		-----
2305. 34	1	4		II		-----
2306. 81	------	2		II		-----
2308. 04	2	------	I			-----
2308. 75	------	2		II		-----
2310. 22	------	70h			III	-----
2310. 92	1	------	I			-----
2312. 82	2	------	I			-----
2313. 437	------	200h			III	-----
2315. 32	3	------	I			-----
2315. 93	4	------	I			-----
2316. 48	4	15hl		II		-----
2318. 49	3	6		II		-----
2319. 08	------	80			III	-----
2319. 21	4	------	I			-----
2319. 54	3	------	I			-----
2320. 98	3	5		II		-----
2321. 153	15	40		II		-----
2322. 471	40	100		II		6
2323. 253	20	50		II		-----
2324. 512	10	20		II		-----
2324. 885	20	50		II		-----
2326. 76	3	------	I			-----
2329. 09	1	2		II		-----
2330. 70	5	------	I			-----
2332. 18	1	1		II		-----
2332. 45	3	7		II		-----
2332. 960	20	30		II		4
2333. 79	1	3hl		II		-----
2334. 10	1	------	I			-----
2335. 24	1	2		II		-----
2335. 50	1	1		II		-----
2335. 772	9	------	I			-----
2336. 467	1	300			III	-----
2336. 693	9	------	I			-----
2337. 335	15	15		II		6
2337. 597	1	------	I			-----
2338. 245	5	8hl		II		-----
2338. 555	7	------	I			-----

Wavelength in air	Intensity		Spectrum			Zeeman type
	Tube	Spark				
A						
2339. 15	3	------	I			-----
2339. 66	1	20			III	-----
2340. 39	3	6hl		II		-----
2340. 59	5	------	I			-----
2342. 06	1	------	I			-----
2342. 40	2	------	I			-----
2343. 320	30	70		II		7
2344. 957	8	------	I			-----
2345. 42	3	5		II		-----
2345. 565	2	------	I			-----
2347. 444	40	100		II		6
2347. 88	1	------	I			-----
2349. 33	2	2h		II		-----
2349. 751	5	------	I			-----
2350. 48	2	------	I			-----
2351. 211	50	150		II		6
2352. 04	8	------	I			-----
2352. 60	5	------	I			-----
2353. 02	10	1	I			-----
2353. 31	1	------	I			-----
2353. 506	1	------	I			-----
2355. 38	5	------	I			-----
2355. 48	------	150h			III	-----
2355. 65	2	------	I			-----
2355. 78	3	------	I			-----
2356. 55	------	1h		II		-----
2357. 05	3	------	I			-----
2358. 01	8	------	I			-----
2358. 90	10	------	I			-----
2359. 08	2	------	I			-----
2359. 27	3	------	I			-----
2360. 29	5	2Hl	I			-----
2360. 29	5	2Hl		II		-----
2361. 290	1	------	I			-----
2362. 02	1	------	I			-----
2362. 34	4	5Hl		II		-----
2362. 394	7	10hl		II		-----
2362. 546	4	------	I			-----
2363. 23	8	------	I			-----
2363. 39	10	------	I			-----
2365. 45	1	------	I			-----
2365. 982	15	20		II		7
2366. 365	9	------	I			-----
2366. 814	8	------	I			-----
2367. 20	1	------	I			-----
2367. 64	2	3		II		-----
2368. 48	10	10hl		II		-----
2370. 44	1	------	I			-----
2370. 92	2	------	I			-----
2371. 41	8	15		II		-----
2371. 54	3	------	I			-----
2371. 92	6	4Hl	I	II?		-----
2372. 23	2	------	I			-----
2372. 348	7	10		II		-----
2373. 12	2	------	I			-----
2373. 296	1	100			III	-----
2373. 530	8	------	I			-----
2374. 186	15	------	I			-----
2374. 516	2	------	I			-----
2375. 937	6	------	I			-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
2376. 46	1	------	I	-----
2377. 237	2	------	I	-----
2377. 471	4	------	I	-----
2377. 57	1	120	III	-----
2377. 98	3	------	I	-----
2378. 163	15	------	I	-----
2378. 32	1	------	I	-----
2378. 513	1	------	I	-----
2378. 81	4	3hl	I II	-----
2378. 925	4	------	I	-----
2379. 716	5	------	I	-----
2380. 305	50	100	II	7
2381. 002	30	60	II	7
2381. 51	1	1	I II	-----
2382. 047	2	3	II	-----
2382. 980	15	------	I	-----
2383. 540	1	250	III	-----
2384. 467	15	------	I	-----
2385. 180	3	4Hl	II	-----
2385. 79	2	3	II	-----
2386. 014	1	------	I	-----
2386. 33	3	6Hl	II	-----
2386. 562	2	------	I	-----
2386. 70	1	------	I	-----
2387. 38	5	------	I	-----
2387. 89	------	6h	III	-----
2388. 50	2	------	I	-----
2390. 20	4	------	I	-----
2390. 794	8	------	I	-----
2392. 008	3	4hl	II	-----
2393. 185	40	60	II	4
2393. 37	80	100	II	4
2393. 828	100	150	II	5
2394. 973	2	------	I	-----
2395. 625	2	3	II	-----
2396. 02	1	1	II	-----
2396. 98	4	------	I	-----
2397. 21	2	------	I	-----
2397. 565	10	------	I	-----
2397. 780	20	------	I	-----
2398. 121	10	------	I	-----
2399. 144	6	------	I	-----
2399. 726	20	------	I	-----
2400. 325	2	------	I	-----
2400. 804	30	80	II	7
2401. 31	2	2h	II	-----
2401. 522	1	------	I	-----
2402. 02	4	10hl	II	-----
2403. 12	8	------	I	-----
2403. 296	4	------	I	-----
2403. 606	10	20	II	5
2404. 566	24	60	II	6
2405. 421	250	400	II	4
2405. 679	3	------	I	-----
2406. 051	5	------	I	-----
2406. 440	50	100	II	-----
2407. 132	9	------	I	-----
2407. 692	20	------	I	-----
2409. 140	2	------	I	-----
2409. 54	2	------	I	-----
A				
2410. 137	200	300	II	6
2410. 97	3	------	I	-----
2411. 14	2	3hl	II	-----
2411. 425	8	------	I	-----
2411. 605	15	3	I	-----
2412. 036	4	5h	II	-----
2412. 261	2	------	I	-----
2412. 51	7	------	I	-----
2412. 622	6	------	I	-----
2412. 85	4	------	I	-----
2413. 348	20	60	II	-----
2413. 871	4	------	I	-----
2414. 045	1	------	I	-----
2415. 11	2	4Hl	II	-----
2415. 59	3	------	I	-----
2415. 72	5	------	I	-----
2415. 84	4	------	I	-----
2415. 965	15	30	II	6
2416. 427	15	1	I	-----
2416. 504	6	------	I	-----
2416. 886	3	5Hl	II	-----
2417. 030	4	------	I	-----
2417. 26	------	20	III	-----
2417. 690	200	300	II	7
2418. 074	2	------	I	-----
2418. 29	1	------	I	-----
2418. 76	1	------	I	-----
2419. 17	2	------	I	-----
2419. 371	2	------	I	-----
2420. 08	1	------	I	-----
2420. 22	2	5hl	II	-----
2420. 554	2	------	I	-----
2420. 78	3	9hl	II	-----
2422. 09	20	------	I	-----
2422. 856	4	5hl	II	-----
2423. 73	2	4hl	II	-----
2424. 003	15	30hl	II	-----
2424. 92	1	------	I	-----
2425. 975	100	200	II	6
2426. 52	5	------	I	-----
2426. 804	9	------	I	-----
2426. 86	7	20hl	II	-----
2428. 740	30	------	I	-----
2428. 993	50	200	II	5
2430. 144	20	3	I II	-----
2430. 92	2	------	I	-----
2431. 152	1	------	I	-----
2431. 414	5	------	I	-----
2432. 303	2	------	I	-----
2432. 854	1	3h	II	-----
2433. 216	2	------	I	-----
2433. 564	60	300	II	4
2433. 798	9	------	I	-----
2433. 88	1	2	II	-----
2434. 266	2	------	I	-----
2434. 522	1	------	I	-----
2434. 764	30	80	II	7
2435. 472	3	------	I	-----
2435. 767	2	------	I	-----
2436. 16	7	10hl	II	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
2437.00	2	3hl	II	-----
2437.79	3	------	I	-----
2438.316	5	------	I	-----
2438.535	9	------	I	-----
2440.814	15	------	I	-----
2441.05	20	40hl	II	-----
2441.22	1	------	I	-----
2441.28	------	10	II	-----
2441.53	1	------	I	-----
2441.920	30	1	I	-----
2443.27	2	5hl	II	-----
2443.766	6	------	I	-----
2444.994	50	1	I	-----
2445.58	4	9Hl	II	-----
2446.248	2	------	I	-----
2446.731	7	3hl	I II	-----
2447.251	200	500	II	6
2447.65	1	------	I	-----
2448.216	------	15h	III	-----
2448.624	1	------	I	-----
2449.053	6	------	I	-----
2449.440	80	200	II	6
2450.05	4	5hl	II	-----
2450.080	10	------	I	-----
2450.66	1	------	I	-----
2451.885	20	------	I	-----
2452.296	20	40	II	4
2452.474	------	80	III	-----
2453.013	30	------	I	-----
2453.336	60	300	II	7
2453.990	20	60	II	6
2455.200	10	20	II	6
2455.711	1	------	I	-----
2456.061	30	------	I	-----
2456.31	1	------	I	-----
2456.65	8	10Hl	II	-----
2456.957	4	------	I	-----
2457.871	15	------	I	-----
2458.653	30	------	I	-----
2459.470	15	20	II	-----
2460.493	200	500	II	6
2461.12	1	------	I	-----
2461.602	3	------	I	-----
2461.74	------	400	III	-----
2462.76	9	10Hl	II	-----
2462.926	4	------	I	-----
2463.378	3	------	I	-----
2463.547	6	------	I	-----
2463.725	3	------	I	-----
2463.933	40	100	II	6
2464.193	200	600	II	7
2464.83	1	------	I	-----
2465.059	50	150	II	-----
2465.46	1	------	I	-----
2465.676	30	1	I	-----
2466.464	8	------	I	-----
2466.665	10	------	I	-----
2467.518	6	------	I	-----
2467.966	60	100	II	5
2468.378	15	------	I	-----

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
2469.179	150	500	II	4
2469.965	15	------	I	-----
2470.998	20	------	I	-----
2471.21	10	5Hl	I II	-----
2471.77	6	6Hl	II	-----
2471.84	------	1h	II	-----
2471.92	7	------	I	-----
2472.54	6	3hl	I II	-----
2472.89	1	------	I	-----
2473.00	1	------	I	-----
2473.736	4	------	I	-----
2473.908	50	200	II	-----
2474.089	15	30	II	4
2475.573	9	------	I	-----
2476.05	6	10hl	II	-----
2476.20	1	------	I	-----
2476.36	3	2h	I II	-----
2476.92	3	4Hl	II	-----
2478.542	20	50	II	5
2479.076	3	------	I	-----
2479.428	20	------	I	-----
2479.76	1	------	I	-----
2480.57	1	------	I	-----
2481.436	30	100	II	5
2481.96	3	3h	II	-----
2482.010	20	------	I	-----
2482.518	3	5	II	-----
2482.647	40	2	I	-----
2482.934	15	------	I	-----
2483.346	50	80	II	5
2484.990	10	------	I	-----
2485.354	3	------	I	-----
2485.555	20	------	I	-----
2485.83	3	8Hl	II	-----
2486.09	3	4hl	II	-----
2487.153	60	2	I	-----
2487.90	3	3Hl	II	-----
2488.14	4	------	I	-----
2488.867	6	------	I	-----
2489.236	15	------	I	-----
2489.892	2	------	I	-----
2490.237	3	4h	II	-----
2490.650	2	------	I	-----
2490.89	9	30Hl	II	-----
2491.058	3	------	I	-----
2491.156	2	------	I	-----
2491.64	1	------	I	-----
2491.871	2	------	I	-----
2492.919	3	3h	II	-----
2493.06	5	------	I	-----
2493.25	------	3h	II	-----
2493.61	1	------	I	-----
2494.364	30	40Hl	II	6
2494.74	2	------	I	-----
2495.16	5	2000	III	-----
2495.675	1	------	I	-----
2496.058	40	1	I	-----
2496.818	30	------	I	-----
2496.991	100	500	II	5
2497.730	8	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
2497. 914	3	------	I	-----	2529. 14	1	------	I	-----
2498. 168	1	------	I	-----	2529. 554	3	------	I	-----
2498. 56	10	10hl	II	-----	2529. 78	10	20Hl	II	7
2498. 70	2	5	II	-----	2531. 196	200	1000	II	5
2499. 32	1	------	I	-----	2531. 73	2	------	I	-----
2499. 825	20	------	I	-----	2531. 94	3	------	I	-----
2500. 096	2	------	I	-----	2532. 12	5	3Hl	I II	-----
2500. 178	1	------	I	-----	2532. 578	30	1	I	-----
2500. 739	30	500	II	4	2532. 94	30	------	I	-----
2501. 130	20	------	I	-----	2532. 972	20	30	II	5
2501. 234	10	------	I	-----	2533. 60	3	------	I	-----
2501. 32	4	------	I	-----	2533. 926	1	------	I	-----
2501. 36	3	5hl	II	-----	2534. 29	2	------	I	-----
2501. 702	1	------	I	-----	2534. 33	2	100	III	-----
2502. 25	2	------	I	-----	2534. 774	8	------	I	-----
2502. 663	50	------	I	-----	2535. 045	10	------	I	-----
2502. 97	2	------	I	-----	2535. 526	2	------	I	-----
2503. 28	1	------	I	-----	2537. 115	10	------	I	-----
2503. 83	3	4Hl	II	-----	2537. 337	50	400	II	4
2504. 13	3	4Hl	II	-----	2538. 266	2	------	I	-----
2505. 18	10	15hl	II	-----	2539. 00	1	------	I	-----
2506. 21	5	10Hl	II	-----	2540. 338	3	------	I	-----
2506. 25	10	15Hl	II	-----	2540. 73	1	2hl	II	-----
2506. 535	9	------	I	-----	2540. 815	3	------	I	-----
2507. 42	3	3hl	II	-----	2541. 062	2	2hl	II	-----
2508. 038	2	------	I	-----	2541. 195	2	2h	II	-----
2509. 790	2	------	I	-----	2542. 12	6	------	I	-----
2509. 892	3	------	I	-----	2543. 12	8	15Hl	II	-----
2510. 38	10	20	II	5	2543. 92	5	9Hl	II	-----
2510. 76	3	------	I	-----	2544. 62	2	------	I	-----
2511. 36	5	------	I	-----	2544. 664	2	2Hl	II	-----
2512. 702	200	800	II	5	2544. 82	2	2Hl	II	-----
2512. 963	100	300	II	-----	2544. 87	3	------	I	-----
2513. 033	200	1000	II	7	2545. 330	60	1	I	-----
2515. 16	3	1000	III	-----	2545. 98	2	------	I	-----
2515. 486	50	400	II	4	2547. 802	3	------	I	-----
2516. 886	300	2000	II	7	2548. 187	50	300	II	7
2517. 52	15	------	I	-----	2548. 528	10	10	I II	-----
2517. 858	30	------	I	7	2548. 971	6	10	II	-----
2518. 36	1	------	I	-----	2549. 141	8	15	II	-----
2518. 59	3	3hl	II	-----	2549. 53	1	------	I	-----
2519. 46	2	2hl	II	-----	2549. 93	1	------	I	-----
2520. 41	8	------	I	-----	2550. 46	1	------	I	-----
2520. 425	20	30Hl	II	-----	2550. 73	2	------	I	-----
2521. 486	40	100	II	5	2551. 38	80	500	II	7
2521. 695	10	------	I	-----	2551. 428	40	300	II	4
2522. 220	3	------	I	-----	2551. 848	20	30	II	5
2522. 749	1	------	I	-----	2552. 36	------	50h	III	-----
2522. 85	3	------	I	-----	2552. 66	2	------	I	-----
2523. 552	2	------	I	-----	2553. 402	10	------	I	-----
2523. 648	------	70h	III	-----	2553. 71	3	3hl	II	-----
2523. 79	3	------	I	-----	2553. 89	2	------	I	-----
2523. 901	3	5h	II	-----	2554. 31	1	------	I	-----
2524. 64	20	------	I	-----	2554. 502	1	2	II	-----
2525. 32	20	30Hl	II	-----	2554. 502	1	2	II	-----
2526. 236	4	------	I	-----	2555. 05	10	------	I	-----
2526. 33	2	10Hl	II	-----	2555. 08	4	5h	II	-----
2527. 43	3	------	I	-----	2555. 32	2	8Hl	II	-----
2527. 87	10	------	I	-----	2556. 39	5	8Hl	II	-----
2528. 25	2	4Hl	II	-----	2556. 924	20	2hl	I II	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
2557. 41	2	------	I	-----
2558. 21	6	------	I	-----
2559. 018	60	2	I	-----
2559. 20	80	500	II	4
2559. 834	2	------	I	-----
2560. 372	1	------	I	-----
2560. 74	------	400h	III	-----
2561. 30	20	------	I	-----
2561. 82	7	10hl	II	-----
2562. 448	2	------	I	-----
2562. 80	10	20hl	II	-----
2563. 613	100	400	II	6
2564. 386	6	------	I	-----
2564. 844	2	4hl	II	-----
2565. 194	15	------	I	-----
2565. 238	4	6	II	-----
2565. 90	8	------	I	-----
2566. 244	10	------	I	-----
2566. 351	8	------	I	-----
2566. 635	15	30Hl	II	-----
2567. 05	2	------	I	-----
2567. 288	7	------	I	-----
2567. 418	20	------	I	-----
2567. 46	2	300h	III	-----
2567. 950	15	------	I	-----
2568. 69	2	------	I	-----
2569. 860	20	------	I	-----
2570. 395	8	------	I	-----
2570. 701	30	100	II	6
2571. 118	10	10Hl	II	-----
2571. 678	300	2000	II	6
2572. 24	2	------	I	-----
2572. 42	2	2	II	-----
2572. 775	30	------	I	-----
2572. 937	15	40	II	4
2573. 912	150	1000	II	6
2574. 28	10	30	II	-----
2574. 896	50	2	I	3
2575. 483	15	30Hl	II	7
2576. 410	2	------	I	-----
2576. 830	150	800	II	5
2577. 55	2	4hl	II	-----
2578. 155	150	600	II	6
2579. 07	8	10Hl	II	-----
2579. 752	1	------	I	-----
2580. 08	7	6Hl	II	-----
2580. 820	20	------	I	-----
2581. 21	2	2h	II	-----
2581. 688	2	2h	II	-----
2581. 924	3	------	I	-----
2582. 508	200	700	II	6
2582. 786	10	------	I	-----
2582. 89	1	30h	III	-----
2582. 982	3	------	I	-----
2584. 06	2	2h	II	-----
2584. 411	2	------	I	-----
2585. 068	1	------	I	-----
2585. 268	1	------	I	-----
2585. 552	2	------	I	-----
2585. 697	2	------	I	-----

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
2586. 118	30	------	I	-----
2586. 72	3	------	I	-----
2586. 80	2	2h	II	-----
2587. 49	2	------	I	-----
2587. 53	1	5hl	II	-----
2587. 674	1	------	I	-----
2588. 536	4	------	I	-----
2588. 668	3	------	I	-----
2589. 472	15	------	I	-----
2589. 776	5	------	I	-----
2589. 842	10	------	I	-----
2590. 277	2	2h	II	-----
2591. 329	100	300	II	5
2592. 162	10	------	I	-----
2593. 334	1	1h	II	-----
2593. 420	3	30	II	-----
2593. 458	5	------	I	-----
2594. 131	50	2	I	-----
2595. 584	10	50	II	6
2595. 807	3	------	I	-----
2596. 35	7	8Hl	II	-----
2596. 67	6	8hl	II	-----
2597. 522	2	------	I	-----
2597. 811	15	------	I	-----
2598. 432	2	------	I	-----
2598. 804	1	------	I	-----
2599. 197	30	200	II	4
2599. 39	3	------	I	-----
2600. 230	2	------	I	-----
2600. 736	2	------	I	-----
2601. 295	3	3h	II	-----
2601. 842	8	------	I	-----
2602. 663	60	3	I	-----
2602. 863	30	2	I	-----
2603. 404	2	------	I	-----
2603. 555	8	------	I	-----
2603. 92	3	------	I	-----
2606. 018	20	------	I	-----
2606. 375	200	1500	II	4
2607. 032	250	2000	II	6
2607. 246	50	200	II	5
2608. 450	60	5	I	3
2608. 628	30	1	I	-----
2609. 13	2	------	I	-----
2609. 274	6	20h	II	-----
2609. 559	1	------	I	-----
2609. 713	2	------	I	-----
2609. 959	40	4	I	-----
2610. 742	2	------	I	-----
2610. 940	3	4hl	II	-----
2611. 340	30	1	I	-----
2611. 617	3	------	I	-----
2612. 585	40	1	I	7
2613. 604	200	1500	II	6
2614. 294	20	100	II	5
2614. 664	2	2h	II	-----
2616. 164	1	2hl	II	-----
2616. 606	80	8	I	1
2617. 048	4	------	I	-----
2617. 15	3	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
2617.649	2	3hl	II	-----	2649.440	4	------	I	-----
2617.804	5	------	I	-----	2649.864	3	------	I	-----
2618.424	2	------	I	-----	2650.022	2	------	I	-----
2619.46	2	------	I	-----	2650.28	------	50	III	-----
2620.33	1	------	I	-----	2650.737	1	------	I	-----
2620.466	3	------	I	-----	2651.166	100	300	II	7
2620.590	20	2	I	-----	2651.785	3	------	I	-----
2620.772	10	------	I	-----	2652.330	6	20	II	6
2620.930	9	25	II	6	2652.781	50	1	I	-----
2621.781	15	20hl	II	7	2653.040	2	4Hl	II	-----
2622.739	400	2000	II	5	2653.826	30	1	I	-----
2623.318	40	1	I	-----	2654.30	1	------	I	-----
2623.665	4	------	I	-----	2654.35	1	1hl	II	-----
2623.906	3	------	I	-----	2655.03	3	2h	I	-----
2624.308	2	------	I	-----	2655.394	4	5	II	-----
2624.576	5	------	I	-----	2655.657	3	------	I	-----
2624.79	60	5Hl	I II	-----	2655.68	------	2h	II	-----
2625.533	20	40	II	6	2656.95	2	------	I	-----
2626.081	1	------	I	-----	2657.487	50	100	II	4
2626.948	50	100	II	6	2657.847	100	200	II	5
2627.720	1	------	I	-----	2659.130	5	------	I	-----
2627.805	1	1h	II	-----	2659.25	5	5h	II	-----
2628.353	1	------	I	-----	2659.704	------	60	III	-----
2629.490	10	10hl	II	-----	2660.523	3	3h	II	-----
2629.756	3	------	I	-----	2661.15	20	------	I	-----
2629.983	8	------	I	-----	2661.883	200	500	II	5
2630.168	9	15h	II	-----	2662.396	15	------	I	-----
2630.34	2	------	I	-----	2662.994	30	------	I	-----
2630.907	100	3	I	-----	2663.572	3	------	I	-----
2631.518	1	2	II	-----	2663.717	10	------	I	-----
2632.017	6	20h	II	-----	2664.02	6	2h	I II	-----
2632.737	1	------	I	-----	2664.583	1	------	I	-----
2633.42	2d	------	I	-----	2664.786	5	------	I	-----
2633.504	2	------	I	-----	2665.051	9	------	I	-----
2634.248	30	------	I	-----	2665.974	100	300	II	7
2634.425	20	------	I	-----	2666.93	4	3h	II	-----
2635.104	3	------	I	-----	2667.12	2	3h	II	-----
2635.570	40	1	I	-----	2667.514	20	20hl	II	-----
2635.780	60	300	II	5	2668.290	90	6	I	1
2636.686	4	------	I	-----	2669.003	80	200	II	6
2636.997	50	5	I	-----	2669.558	8	20	II	-----
2637.510	2	------	I	-----	2669.924	2	------	I	-----
2637.853	15	------	I	-----	2670.305	3	3	II	-----
2638.712	200	400	II	7	2670.638	1	------	I	-----
2638.975	------	80	III	-----	2670.76	2	------	I	-----
2639.183	40	------	I	-----	2670.895	6	------	I	-----
2639.960	3	------	I	-----	2671.022	2	------	I	-----
2640.121	1	------	I	-----	2671.24	30	100	II	6
2640.829	4	------	I	-----	2671.721	40	1	I	-----
2641.410	300	1000	II	4	2672.122	3	------	I	-----
2642.076	60	2	I	2	2672.454	1	------	I	-----
2642.751	80	6	I	2	2673.007	9	------	I	-----
2643.886	4	------	I	-----	2673.060	5	------	I	-----
2643.999	15	1	I	-----	2673.191	2	------	I	-----
2644.443	4	5Hl	II	-----	2673.542	1	------	I	-----
2645.262	20	1	I	-----	2673.78	1	------	I	-----
2647.294	200	600	II	6	2674.50	1	4hl	II	-----
2648.045	5	5hl	II	-----	2674.80	5	------	I	-----
2649.136	30	100	II	5	2675.250	10	2h	I	-----
2649.397	2	------	I	-----	2675.47	8	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
2675. 957	30	------	I	-----	2706. 734	70	400	II	5
2676. 27	1	------	I	-----	2707. 87	8	------	I	-----
2676. 426	3	------	I	-----	2708. 154	1	------	I	-----
2676. 612	20	100	II	4	2708. 652	2	------	I	-----
2677. 558	15	30	II	5	2709. 166	2	------	I	-----
2677. 914	2	------	I	-----	2709. 702	3	------	I	-----
2677. 99	1	------	I	-----	2709. 963	10	20Hl	II	-----
2678. 403	20	100	II	7	2710. 63	4	8Hl	II	-----
2678. 925	2	------	I	-----	2711. 17	2	------	I	-----
2679. 40	2	------	I	-----	2711. 595	5	------	I	-----
2679. 761	2	------	I	-----	2711. 823	40	5	I	-----
2679. 840	2	2h	II	-----	2711. 93	10	40	II	-----
2680. 592	1	------	I	-----	2712. 00	20	40	II	-----
2680. 770	2	2h	II	-----	2712. 14	10	60	II	-----
2681. 72	4	------	I	-----	2712. 424	50	500	II	7
2682. 180	40	1	I	-----	2712. 96	1	------	I	-----
2683. 269	80	------	I	-----	2713. 49	6	15h	II	7
2683. 350	200	1000	II	6	2713. 837	50	5	I	3
2684. 008	10	20	II	6	2714. 06	15	1	I	-----
2685. 209	50	200	II	7	2714. 56	2	3hl	II	-----
2685. 701	4d	------	I	-----	2715. 423	3	------	I	-----
2685. 72	------	3	II	-----	2716. 55	1	------	I	-----
2686. 360	20	1	I	-----	2716. 87	7	------	I	-----
2686. 547	6	------	I	-----	2717. 36	1	------	I	-----
2686. 88	2	------	I	-----	2717. 54	1	------	I	-----
2687. 220	------	200	III	-----	2717. 87	6	20Hl	II	-----
2687. 846	5	------	I	-----	2718. 445	30	4	I	-----
2688. 360	50	2	I	-----	2718. 496	10	200	II	7
2688. 980	6	------	I	-----	2718. 593	50	10	I	3
2689. 322	3	------	I	-----	2719. 755	10	------	I	-----
2690. 319	7	------	I	-----	2720. 91	1	------	I	-----
2690. 656	1	------	I	-----	2721. 160	3	7Hl	II	-----
2690. 715	------	4H	II	-----	2721. 462	2	------	I	-----
2691. 04	1	------	I	-----	2721. 90	8	------	I	-----
2693. 082	2	------	I	-----	2722. 893	4	------	I	-----
2693. 80	2	------	I	-----	2723. 58	1	2h	II	-----
2694. 058	3	------	I	-----	2723. 99	2	10Hl	II	-----
2694. 460	1	------	I	-----	2726. 70	60	7	I	3
2694. 76	2	------	I	-----	2726. 972	5	------	I	-----
2696. 180	80	10	I	1	2727. 17	5	20hl	II	-----
2696. 552	8	------	I	-----	2727. 644	1	------	I	-----
2696. 77	2	------	I	-----	2727. 797	1	------	I	-----
2697. 157	1	------	I	-----	2728. 10	1	------	I	-----
2697. 70	9	------	I	-----	2728. 22	2	3Hl	II	-----
2698. 054	2	------	I	-----	2729. 098	40	5	I	2
2698. 314	2	------	I	-----	2729. 376	7	------	I	-----
2698. 82	1	------	I	-----	2729. 44	2	4hl	II	-----
2699. 632	70	10	I	7	2729. 88	1	------	I	-----
2700. 12	1	------	I	-----	2730. 13	2	------	I	-----
2700. 834	3	------	I	-----	2730. 700	50	5	I	2
2701. 43	1	------	I	-----	2730. 86	60	6	I	-----
2701. 545	2	------	I	II -----	2731. 154	10	60	II	4
2702. 004	3	------	I	-----	2732. 146	4	------	I	-----
2702. 37	1	------	I	-----	2732. 662	10	40h	II	4
2702. 507	5	10Hl	II	-----	2732. 882	15	100hl	II	-----
2703. 163	10	30	II	4	2733. 310	2	------	I	-----
2704. 34	2	------	I	-----	2735. 099	10	30	II	4
2704. 554	15	------	I	-----	2735. 638	2	------	I	-----
2705. 612	100	20	I	2	2735. 740	3	5Hl	II	7
2706. 645	40	200	II	-----	2736. 024	20	1	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
2737. 150	2	------	I	-----	2770. 94	1	------	I	-----
2737. 816	50	3	I	7	2771. 328	3	------	I	-----
2738. 759	300	1000	II	4	2772. 335	40	200	II	6
2740. 357	10	50Hl	II	6	2773. 021	60	10	I	-----
2741. 067	3	------	I	-----	2773. 360	300	2000	II	4
2741. 46	1	------	I	-----	2773. 500	30	300	II	-----
2742. 091	20	1	I	-----	2774. 018	100	400	II	5
2742. 56	2	2	II	-----	2775. 268	40	100	II	4
2742. 633	7	------	I	-----	2776. 26	3	------	I	-----
2743. 637	100	20	I	3	2776. 62	2	------	I	-----
2744. 23	1	------	I	-----	2776. 93	2	2Hl	II	-----
2744. 51	1	------	I	-----	2777. 281	3	7Hl	II	-----
2745. 095	1	------	I	-----	2778. 20	2	6Hl	II	-----
2746. 163	1	------	I	-----	2778. 40	1	------	I	-----
2746. 606	40	2	I	-----	2778. 884	4	------	I	-----
2746. 940	2	------	I	-----	2779. 370	150	30	I	1
2748. 111	1	------	I	-----	2780. 938	2	------	I	-----
2748. 338	2	------	I	-----	2781. 421	2	------	I	-----
2748. 445	3	3h	II	-----	2781. 53	2	------	I	-----
2748. 68	2	7h	II	-----	2782. 465	15	------	I	-----
2749. 49	2	------	I	-----	2783. 698	60	10	I	3
2749. 51	1	2hl	II	-----	2784. 10	1	------	I	-----
2750. 252	1	------	I	-----	2784. 457	3	10h	II	-----
2750. 677	1	------	I	-----	2785. 874	2	------	I	-----
2750. 89	1	------	I	-----	2786. 314	20	200	II	5
2751. 194	2	15hl	II	-----	2787. 211	10	------	I	-----
2751. 243	5	------	I	-----	2787. 922	3	10h	II	-----
2751. 814	150	500	II	5	2788. 42	1	------	I	-----
2752. 53	3	------	I	-----	2788. 460	3	------	I	-----
2752. 58	1	4Hl	II	-----	2789. 496	100	400	II	7
2753. 60	1	500	III	-----	2789. 714	200	700	II	5
2753. 83	3	------	I	-----	2789. 825	40	100	II	-----
2754. 219	2	------	I	-----	2790. 436	5	10hl	II	-----
2754. 368	1	------	I	-----	2791. 338	3	------	I	-----
2754. 552	1	------	I	-----	2791. 73	1	------	I	-----
2755. 666	2	------	I	-----	2792. 309	3	------	I	-----
2755. 991	10	------	I	-----	2792. 659	3	------	I	-----
2756. 918	60	200	II	6	2792. 800	3	20hl	II	5
2757. 633	2	------	I	-----	2793. 61	2	7Hl	II	-----
2757. 72	1	------	I	-----	2793. 762	5	------	I	-----
2758. 314	40	5	I	-----	2794. 10	1	1	II	-----
2758. 771	80	10	I	2	2794. 703	10	------	I	-----
2759. 08	1	6hl	II	-----	2795. 093	3	2Hl	I II	-----
2759. 635	2	------	I	-----	2795. 747	3	------	I	-----
2760. 006	1	------	I	-----	2795. 826	3	------	I	-----
2761. 165	8	80hl	II	4	2796. 951	1	------	I	-----
2761. 634	200	20	I	7	2797. 980	10	------	I	-----
2761. 78	10	------	I	-----	2798. 440	10	20Hl	II	-----
2762. 688	60	10	I	1	2799. 740	6	10Hl	II	-----
2763. 493	3	------	I	-----	2799. 93	1	------	I	-----
2763. 594	1	------	I	-----	2800. 652	1	------	I	-----
2763. 68	2	------	I	-----	2801. 426	20	------	I	-----
2764. 462	2	10hl	II	-----	2802. 106	6	------	I	-----
2764. 892	10	100	II	6	2802. 479	50	2	I	-----
2765. 048	20	------	I	-----	2802. 73	2	8Hl	II	-----
2766. 301	3	------	I	-----	2803. 29	1	------	I	-----
2766. 966	80	10	I	3	2803. 48	3	------	I	-----
2767. 09	9	------	I	-----	2804. 35	2	5hl	II	-----
2767. 32	10	60hl	II	-----	2805. 00	3	8Hl	II	-----
2770. 438	40	300	II	4	2805. 745	2	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
2806. 275	3	------	I	-----
2806. 624	6	------	I	-----
2806. 80	2	------	I	-----
2807. 49	------	5hl	II	-----
2807. 506	10	------	I	-----
2808. 00	200	1000	II	6
2808. 60	1	------	I	-----
2808. 80	2	------	I	-----
2809. 39	2	------	I	-----
2809. 595	10	15	II	-----
2810. 20	2	3Hl	II	-----
2810. 78	2	------	I	-----
2811. 692	10	------	I	-----
2812. 326	40	3	I	-----
2813. 87	150	600	II	6
2814. 478	100	500	II	6
2814. 762	60	300	II	6
2815. 815	50	2	I	-----
2816. 068	20	60hl	II	4
2816. 88	1	4hl	II	-----
2817. 685	100	10	I	2
2818. 000	2	------	I	-----
2818. 942	60	5	I	3
2819. 194	3	------	I	-----
2819. 746	100	15	I	2
2820. 227	500	2000	II	4
2820. 417	20	100	II	-----
2820. 664	2	------	I	-----
2822. 355	5	------	I	-----
2822. 678	300	1500	II	5
2823. 40	2	------	I	-----
2824. 50	1	------	I	-----
2827. 27	1	------	I	-----
2828. 078	2	------	I	-----
2828. 148	5	20h	II	4
2828. 430	3	------	I	-----
2828. 49	4	------	I	-----
2828. 506	2	4hl	II	-----
2829. 08	2	------	I	-----
2829. 327	40	200	II	7
2830. 511	20	1	I	-----
2830. 985	2	------	I	-----
2831. 934	1	------	I	-----
2832. 54	10	20Hl	II	7
2833. 285	150	20	I	1
2834. 130	60	10	I	2
2835. 140	10	40Hl	II	7
2836. 028	2	------	I	-----
2836. 13	3	------	I	-----
2836. 82	2	------	I	-----
2837. 55	1	------	I	-----
2837. 96	2	------	I	-----
2838. 02	2	------	I	-----
2838. 65	1	------	I	-----
2838. 76	1	5hl	II	-----
2840. 387	15	1	I	-----
2841. 493	70	7	I	7
2841. 884	20	100Hl	II	5
2842. 773	2	------	I	-----
2843. 10	3	------	I	-----
A				
2843. 530	30	1	I	-----
2844. 890	10	------	I	-----
2845. 11	3	------	I	-----
2845. 57	2	------	I	-----
2845. 832	200	20	I	2
2846. 383	5	15Hl	II	-----
2846. 633	9	------	I	-----
2846. 829	1	------	I	-----
2847. 047	2	3hl	II	-----
2847. 21	1	------	I	-----
2847. 656	3	------	I	-----
2849. 215	300	1000	II	5
2849. 648	10	------	I	-----
2850. 156	40	200	II	5
2850. 967	100	20	I	7
2851. 211	200	400	II	6
2852. 018	100	300	II	6
2853. 757	2	------	I	-----
2854. 168	1	------	I	-----
2854. 565	1	------	I	-----
2855. 30	1	------	I	-----
2855. 828	5	------	I	-----
2855. 997	2	------	I	-----
2856. 975	6	20	II	-----
2857. 652	50	100	II	4
2858. 658	10	40	II	4
2859. 103	6	------	I	-----
2859. 66	1	------	I	-----
2859. 97	1	------	I	-----
2860. 314	40	100	II	4
2860. 558	100	15	I	3
2861. 009	500	2000	II	5
2861. 695	600	2500	II	5
2862. 632	20	1	I	-----
2863. 41	60	4	I	2
2863. 64	4	------	I	-----
2864. 722	9	------	I	-----
2865. 054	1	------	I	-----
2865. 422	3	------	I	-----
2865. 562	5	30hl	II	-----
2866. 373	500	100	I	2
2867. 06	2	------	I	-----
2867. 70	60	7	I	-----
2868. 107	15	1	I	-----
2868. 950	4	------	I	-----
2869. 82	80	200	II	5
2870. 744	2	3h	II	-----
2871. 72	2	------	I	-----
2871. 90	------	50h	III	-----
2872. 246	2	------	I	-----
2872. 480	10	------	I	-----
2872. 730	4	------	I	-----
2873. 632	50	3	I	-----
2874. 486	1	------	I	-----
2874. 82	1	------	I	-----
2876. 328	200	1000	II	5
2877. 18	80	7	I	3
2878. 66	10	------	I	-----
2879. 12	30	100	II	4
2879. 418	2	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
2879.72	10	30Hl	II	-----	2918.591	300	40	I	3
2880.211	2	10Hl	II	-----	2919.60	300	2000	II	6
2880.84	1	------	I	-----	2922.15	4	------	I	-----
2882.259	15	------	I	-----	2924.613	150	20	I	7
2882.57	1	------	I	-----	2925.965	10	------	I	-----
2883.02	1	------	I	-----	2926.04	4	20	II	-----
2884.12	1	------	I	-----	2926.22	10	------	I	-----
2885.474	40	200	II	5	2926.328	10	40	II	4
2886.91	10	10hl	II	-----	2926.58	7	------	I	-----
2887.132	200	60	I	1	2927.65	3	------	I	-----
2887.542	100	30	I	2	2928.980	40	6	I	1
2888.23	1	1h	II	-----	2929.642	400	2000	II	7
2888.633	8	------	I	-----	2929.895	200	50	I	1
2889.001	8	50	II	4	2930.55	7	50Hl	II	4
2889.62	300	50	I	1	2930.69	4	------	I	-----
2891.019	40	4	I	-----	2932.92	1	2h	II	-----
2891.46	1	------	I	-----	2934.641	20	1	I	-----
2891.89	2	------	I	-----	2935.365	40	2	I	7
2891.954	3	------	I	-----	2935.725	10	------	I	-----
2892.285	4	5hl	II	-----	2936.338	2	------	I	-----
2892.565	60	7	I	7	2937.782	400	3000	II	6
2892.98	3	------	I	-----	2938.235	4	------	I	-----
2893.03	2	------	I	-----	2938.656	2	------	I	-----
2893.751	10	------	I	-----	2940.23	1	5hl	II	-----
2894.028	10	20h	II	6	2940.762	800	100	I	3
2894.840	30	3	I	-----	2942.73	10	------	I	-----
2896.260	10	------	I	-----	2943.70	2	------	I	-----
2897.11	1	------	I	-----	2944.71	200	40	I	2
2897.34	------	5Sh	III	-----	2947.135	20	300	II	4
2898.256	500	50	I	7	2947.474	2	------	I	-----
2898.702	50	200	II	5	2947.72	2	------	I	-----
2900.12	1	------	I	-----	2948.390	6	------	I	-----
2900.750	20	------	I	-----	2949.58	2	50Hl	II	-----
2901.16	4	------	I	-----	2949.81	5	------	I	-----
2901.31	1	2hl	II	-----	2950.67	600	100	I	3
2901.925	10	------	I	-----	2951.900	20	5	I	-----
2902.641	30	1	I	-----	2952.55	2	5Hl	II	-----
2902.81	10	------	I	-----	2953.12	1	------	I	-----
2904.412	400	70	I	3	2953.36	1	------	I	-----
2904.531	20	100h	II	-----	2953.647	3	30	II	-----
2904.760	300	60	I	1	2954.201	500	100	I	1
2905.17	5	------	I	-----	2954.53	6	------	I	-----
2906.61	1	2h	II	-----	2954.935	2	7	II	-----
2907.012	30	1	I	-----	2955.64	4	------	I	-----
2907.318	3	------	I	-----	2955.99	1	3h	II	-----
2907.63	1	7Hl	II	-----	2956.376	30	1	I	-----
2908.831	10	30Hl	II	5	2957.27	2	20hl	II	-----
2909.912	200	300	II	5	2958.01	300	40	I	3
2910.46	1	------	I	-----	2958.55	4	------	I	-----
2911.836	2	------	I	-----	2959.144	2	20Hl	II	-----
2912.760	10	20	II	4	2960.180	5	------	I	-----
2913.179	10	50hl	II	4	2960.813	20	200	II	5
2913.56	5	------	I	-----	2961.80	40	400	II	6
2913.64	2	------	I	-----	2962.592	1	------	I	-----
2915.08	5	------	I	-----	2962.921	2	------	I	-----
2915.27	5	------	I	-----	2963.547	5	------	I	-----
2915.72	1	------	I	-----	2963.72	2	5Hl	II	-----
2916.48	800	100	I	1	2963.90	1	------	I	-----
2917.308	8	------	I	-----	2963.97	1	------	I	-----
2917.487	20	200	II	5	2964.885	400	80	I	7

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
2965. 46	1	.....	I	.....	3000. 464	6	.....	I	
2966. 054	7	.....	I	.....	3000. 82	2	.....	I	.....
2966. 953	150	30	I	1	3001. 840	4	40	II	6
2967. 230	60	500	II	6	3002. 46	4	.....	I	.....
2967. 85	5	.....	I	.....	3002. 90	20	1	I	.....
2967. 98	1	.....	I	.....	3003. 287	10	.....	I	.....
2968. 338	10	.....	I	.....	3003. 62	2	.....	I	.....
2968. 805	300	2000	II	6	3004. 06	20	.....	I	.....
2968. 94	20	200	II	.....	3004. 337	3	.....	I	.....
2970. 486	4	.....	I	.....	3004. 725	4	10Hl	II	.....
2970. 60	.....	30	III	.....	3005. 556	300	100	I	3
2971. 24	1	.....	I	.....	3005. 84	10	.....	I	.....
2972. 00	2	.....	I	.....	3006. 39	10	.....	I	.....
2972. 805	4	.....	I	.....	3006. 83	1	.....	I	.....
2973. 058	20	.....	I	.....	3007. 03	2	.....	I	.....
2973. 390	100	30	I	1	3007. 49	3	.....	I	.....
2974. 07	20	70	II	6	3008. 63	3	10Hl	II	.....
2975. 886	600	3000	II	7	3009. 86	10	1	I	.....
2976. 394	10	.....	I	.....	3010. 251	4	.....	I	.....
2977. 109	6	.....	I	.....	3010. 97	3	.....	I	.....
2977. 587	30	500	II	7	3011. 214	15	300	II	5
2979. 288	100	30	I	2	3012. 19	3	20	II	5
2979. 934	4	.....	I	.....	3012. 893	400	3000	II	5
2980. 204	2	40	II	5	3014. 10	1	.....	I	.....
2980. 815	500	100	I	3	3014. 84	10	.....	I	.....
2981. 43	1	.....	I	.....	3014. 947	2	10Hl	II	.....
2981. 81	1	.....	I	.....	3015. 90	1	.....	I	.....
2982. 43	10	.....	I	.....	3016. 28	2	.....	I	.....
2982. 56	3	.....	I	.....	3016. 69	150	40	I	2
2982. 727	150	40	I	7	3016. 80	200	50	I	1
2984. 058	50	10	I	2	3016. 96	20	100	II	4
2984. 352	2	10Hl	II	.....	3017. 36	30	4	I	.....
2984. 456	7	.....	I	.....	3017. 80	2	.....	I	.....
2985. 80	1	.....	I	.....	3018. 30	250	70	I	3
2985. 938	2	.....	I	.....	3019. 37	1	.....	I	.....
2986. 74	1	.....	I	.....	3019. 78	2	.....	I	.....
2986. 943	1	5Hl	II	.....	3020. 01	1	.....	I	.....
2987. 244	7	.....	I	.....	3020. 530	300	100	I	3
2987. 62	5	.....	I	.....	3020. 99	10	.....	I	.....
2988. 576	5	.....	I	.....	3022. 10	10	100	II	4
2989. 46	8	.....	I	.....	3023. 118	10	.....	I	.....
2989. 76	1	.....	I	.....	3024. 335	2	6h	II	.....
2990. 228	4	.....	I	.....	3024. 592	50	4	I	.....
2990. 800	10	80	II	4	3024. 780	40	200	II	4
2991. 756	2	.....	I	.....	3025. 287	80	300	II	5
2992. 074	30	5	I	.....	3026. 61	2	.....	I	.....
2992. 624	1	6Hl	II	.....	3028. 111	4	.....	I	.....
2993. 011	3	.....	I	.....	3029. 446	20	1	I	.....
2993. 413	2	10Hl	II	7	3030. 36	1	.....	I	.....
2993. 647	3	.....	I	.....	3031. 159	300	2000	II	5
2993. 86	2	.....	I	.....	3031. 566	3	.....	I	.....
2994. 036	8	.....	I	.....	3031. 790	20	.....	I	.....
2994. 43	1	.....	I	.....	3032. 48	10	.....	I	.....
2995. 76	1	.....	I	.....	3034. 21	7	.....	I	.....
2996. 278	6	.....	I	.....	3034. 556	30	3	I	.....
2996. 731	5	20Hl	II	7	3035. 23	2	30Hl	II	.....
2998. 44	1	.....	I	.....	3036. 773	10	1	I	.....
2999. 32	2	.....	I	.....	3037. 28	30	.....	I	.....
2999. 523	20	.....	I	.....	3037. 63	6	.....	I	.....
3000. 092	300	1000	II	4	3038. 666	15	1	I	.....

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
3039. 025	7	------	I	-----
3039. 647	15	------	I	-----
3039. 70	3	10Hl	II	-----
3041. 004	2	------	I	-----
3041. 41	9	------	I	-----
3042. 085	30	4	I	1
3042. 271	20	------	I	-----
3042. 552	15	------	I	-----
3042. 654	3	15Hl	II	-----
3043. 30	3	------	I	-----
3043. 905	10	------	I	-----
3044. 103	20	1	I	-----
3045. 28	1	------	I	-----
3045. 40	2	------	I	-----
3046. 030	40	400	II	4
3046. 68	1	------	I	-----
3047. 492	20	1	I	-----
3049. 06	3	------	I	-----
3049. 300	60	15	I	3
3049. 74	1	3h	II	-----
3050. 760	300	80	I	2
3051. 16	5	------	I	-----
3051. 30	10	------	I	-----
3052. 75	1	------	I	-----
3053. 28	2	4	II	-----
3053. 74	1	------	I	-----
3054. 53	100	300	II	6
3055. 415	30	400	II	5
3056. 702	20	2	I	-----
3057. 010	400	100	I	3
3057. 59	7	------	I	-----
3058. 31	2	------	I	-----
3058. 61	3	------	I	-----
3058. 66	1	1h	II	-----
3058. 77	1	------	I	-----
3059. 343	10	------	I	-----
3060. 084	------	100h	III	-----
3060. 18	1	------	I	-----
3063. 778	80	10	I	7
3064. 355	5	20	II	-----
3064. 686	40	500	II	5
3066. 18	30	1	I	-----
3066. 515	5	30Hl	II	-----
3067. 426	200	40	I	1
3067. 614	60	10	I	-----
3068. 18	15	1	I	-----
3069. 213	80	15	I	1
3069. 645	2	10	II	-----
3069. 726	7	------	I	-----
3069. 804	2	------	I	-----
3069. 950	8	70Hl	II	-----
3070. 095	20	------	I	-----
3070. 498	15	------	I	-----
3070. 85	1	------	I	-----
3071. 77	10	------	I	-----
3072. 365	20	------	I	-----
3072. 881	400	100	I	2
3073. 48	10	------	I	-----
3074. 104	60	20	I	3
3074. 789	100	40	I	2
3075. 315	40	7	I	-----
3075. 874	20	1	I	-----
3076. 665	4	100	II	6
3076. 885	30	1	I	-----
3077. 76	2	------	I	-----
3078. 04	2	------	I	-----
3078. 77	6	------	I	-----
3079. 10	2	3Hl	II	-----
3080. 27	4	------	I	-----
3080. 635	100	2000	II	6
3080. 842	200	50	I	1
3081. 844	7	------	I	-----
3082. 14	6	------	I	-----
3082. 526	7	------	I	-----
3083. 085	8	------	I	-----
3083. 151	15	------	I	-----
3083. 53	3	30Hl	II	-----
3083. 628	30	------	I	-----
3084. 743	20	------	I	-----
3085. 17	2	------	I	-----
3086. 580	2	------	I	-----
3087. 196	60	6	I	-----
3087. 947	8	1	I	-----
3088. 533	60	5	I	-----
3088. 985	4	------	I	-----
3089. 39	1	------	I	-----
3089. 527	7	------	I	-----
3090. 170	30	1	I	-----
3090. 516	20	------	I	-----
3091. 397	40	6	I	-----
3091. 770	8	80hl	II	6
3092. 250	60	500hl	II	5
3093. 65	1	2	II	-----
3095. 186	4	------	I	-----
3096. 764	150	40	I	3
3097. 602	3	------	I	-----
3098. 482	3	------	I	-----
3098. 59	1	------	I	5
3099. 085	2	20Hl	II	-----
3100. 47	2	------	I	-----
3100. 792	30	1	I	-----
3101. 391	300	1000	II	5
3102. 391	8	------	I	-----
3103. 19	1	------	I	-----
3103. 410	------	15h	III	-----
3103. 66	20	------	I	-----
3103. 712	50	1	I	-----
3104. 49	1	4h	II	-----
3104. 822	10	------	I	-----
3105. 51	2	------	I	-----
3106. 01	2	------	I	-----
3106. 14	1	1h	II	-----
3106. 43	1	------	I	-----
3106. 51	2	------	I	-----
3106. 75	1	------	I	-----
3106. 93	1	------	I	-----
3107. 815	3	7Hl	II	-----
3107. 91	2	------	I	-----
3108. 043	10	------	I	-----
3108. 63	2	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
3109. 121	400	2000	II	6
3109. 852	4	------	I	-----
3110. 882	50	400	II	4
3111. 472	4	20	II	-----
3111. 99	1	------	I	-----
3112. 43	1	2hl	II	-----
3112. 82	1	------	I	-----
3113. 447	7	------	I	-----
3113. 68	2	3hl	II	-----
3114. 059	1	------	I	-----
3114. 56	2	------	I	-----
3114. 896	15	------	I	-----
3116. 19	1	------	I	-----
3116. 506	30	------	I	-----
3116. 947	20	200	II	6
3118. 33	10	------	I	-----
3118. 63	2	------	I	-----
3118. 77	4	------	I	-----
3119. 24	1	------	I	-----
3119. 31	2	------	I	-----
3119. 980	100	40	I	7
3120. 645	15	1	I	-----
3122. 09	1	6Hl	II	-----
3122. 322	7	------	I	-----
3122. 55	2	------	I	-----
3122. 87	------	7h	II	-----
3122. 948	10	------	I	-----
3123. 51	1	------	I	-----
3123. 68	1	------	I	-----
3123. 973	1	------	I	-----
3124. 510	20	1	I	-----
3124. 89	1	------	I	-----
3126. 278	20	100	II	5
3126. 655	20	4	I	-----
3126. 95	5	------	I	-----
3127. 390	10	------	I	-----
3128. 760	100	20	I	-----
3129. 588	80	15	I	-----
3130. 40	3	------	I	-----
3130. 60	1	2hl	II	-----
3131. 812	400	200	I	7
3132. 236	20	3	I	-----
3133. 03	1	------	I	-----
3133. 078	3	60	II	-----
3133. 30	1	------	I	-----
3133. 83	1	------	I	-----
3134. 725	600	5000	II	6
3135. 562	30	2	I	-----
3135. 770	20	1	I	-----
3137. 520	70	30	I	1
3138. 43	20	1	I	-----
3138. 651	200	20	I	-----
3139. 29	4	------	I	5
3139. 663	100	500	II	7
3140. 771	40	500	II	-----
3142. 57	1	------	I	-----
3144. 46	7	------	I	-----
3145. 315	200	500	II	6
3146. 22	2	------	I	-----
3146. 95	------	40h	III	-----
3147. 22	2	------	I	-----
3147. 28	4	------	I	-----
3148. 10	3	------	I	-----
3148. 415	100	40	I	1
3148. 898	5	------	I	-----
3149. 064	20	2	I	-----
3149. 824	15	1	I	-----
3150. 332	15	1	I	-----
3151. 64	80	20	I	2
3151. 962	8	------	I	-----
3152. 59	20	2	I	-----
3152. 841	7	------	I	-----
3152. 952	30	6	I	-----
3153. 52	3	------	I	-----
3154. 64	2	------	I	-----
3156. 48	20	2	I	-----
3156. 688	200	100	I	2
3157. 08	3	------	I	-----
3158. 44	1	------	I	-----
3158. 71	4	------	I	-----
3158. 82	7	------	I	-----
3159. 84	300	40	I	2
3159. 96	10	50	II	-----
3160. 231	10	------	I	-----
3161. 09	2	------	I	-----
3161. 23	1	------	I	-----
3161. 536	20	3	I	3
3162. 575	300	30	I	3
3162. 624	100	500	II	7
3163. 360	30	3	I	-----
3163. 90	3	5hl	II	-----
3164. 385	100	20	I	7
3165. 27	1	------	I	-----
3165. 730	50	10	I	7
3166. 97	3	------	I	-----
3167. 15	1	------	I	-----
3167. 454	10	30	II	-----
3168. 26	8	------	I	-----
3168. 390	100	40	I	7
3168. 957	2	3hl	II	-----
3169. 50	------	7hl	II	-----
3169. 60	4	------	I	-----
3169. 762	10	------	I	-----
3170. 83	2	------	I	-----
3172. 08	1	------	I	-----
3172. 24	6	------	I	-----
3172. 949	300	70	I	3
3173. 65	1	4hl	II	-----
3174. 882	30	6	I	3
3175. 957	10	------	I	-----
3176. 858	200	600	II	4
3178. 05	10	------	I	-----
3178. 436	40	5	I	1
3179. 62	40	5	I	-----
3180. 19	10	------	I	-----
3180. 81	20	2	I	-----
3181. 008	80	10	I	7
3181. 148	70	10	I	1
3181. 756	5	50	II	5
3182. 57	2	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
3182.742	10	.....	I	.....	3216.94	10	.....	I	.....
3183.18	1	.....	I	.....	3217.289	100	200	II	5
3183.27	1	.....	I	.....	3218.165	5	100	II	7
3183.67	2	8hl	II	.....	3218.770	70	5	I	1
3184.056	20	2	I	.....	3220.032	10	.....	I	.....
3184.51	1	.....	I	.....	3220.650	100	500	II	5
3185.03	4	.....	I	.....	3222.538	30	1	I	.....
3185.307	4	10Hl	II	5	3223.45	1	.....	I	.....
3186.04	1	.....	I	.....	3223.864	5	15hl	II	.....
3186.26	2	5Hl	II	.....	3224.77	1	.....	I	.....
3186.44	3	.....	I	.....	3225.020	5	50hl	II	7
3187.15	2	.....	I	.....	3225.78	1	.....	I	.....
3189.632	100	20	I	2	3226.44	5	15Hl	II	.....
3190.27	3	.....	I	.....	3226.991	10	50	II	4
3191.938	10	.....	I	.....	3227.868	40	3	I	.....
3192.362	7	.....	I	.....	3228.320	2	.....	I	.....
3193.16	10	.....	I	.....	3228.43	1	.....	I	.....
3193.530	200	1000	II	6	3229.493	15	1	I	.....
3194.199	400	2000	II	5	3230.058	100	10	I	7
3194.486	10	50	II	.....	3232.204	20	2	I	.....
3194.776	20	.....	I	.....	3232.593	1	.....	I	.....
3195.162	5	.....	I	.....	3232.999	2	.....	I	.....
3195.630	20	100	II	5	3233.23	1	.....	I	.....
3195.87	10	.....	I	.....	3233.797	4	40h	II	4
3196.10	4	.....	I	.....	3234.11	7	10Hl	II	.....
3196.916	60	10	I	7	3235.25	4	.....	I	.....
3197.39	2	.....	I	.....	3235.80	2	.....	I	.....
3198.00	2	.....	I	.....	3235.878	1	5Hl	II	.....
3198.310	2	7Hl	II	.....	3236.76	100	10	I	2
3198.69	2	.....	I	.....	3238.274	10	.....	I	.....
3198.841	10	.....	I	.....	3238.38	2	7Hl	II	.....
3199.262	20	2	I	.....	3239.010	20	2	I	.....
3199.996	40	300	II	6	3239.393	80	8	I	7
3200.40	8	.....	I	.....	3240.62	4	.....	I	.....
3201.020	20	1	I	.....	3240.77	7	.....	I	.....
3201.065	10	.....	I	.....	3240.991	80	15	I	.....
3202.149	10	80	II	6	3241.734	9	.....	I	.....
3202.37	10	.....	I	.....	3242.130	30	2	I	.....
3202.74	30	2	I	.....	3242.42	1	7hl	II	.....
3203.10	10	1	I	.....	3242.98	5	100	II	5
3203.657	30	100	II	4	3243.343	100	10	I	7
3204.39	1	.....	I	.....	3243.735	7	.....	I	.....
3205.545	10	1	I	.....	3243.82	2	5hl	II	.....
3206.108	150	30	I	2	3244.42	4	.....	I	.....
3206.741	5	80h	II	5	3244.66	1	.....	I	.....
3206.80	7	.....	I	.....	3245.472	10	.....	I	.....
3207.51	1	1hl	II	.....	3245.960	15	.....	I	.....
3207.77	1	.....	I	.....	3246.923	40	2	I	.....
3208.12	2	.....	I	.....	3247.67	400	80	I	3
3209.21	5	.....	I	.....	3247.88	30	3	I	.....
3209.25	5	.....	I	.....	3248.41	.....	6h	II	.....
3209.757	3	.....	I	.....	3248.49	10	1	I	.....
3210.70	10	.....	I	.....	3249.154	7	.....	I	.....
3210.965	100	10	I	7	3249.529	200	20	I	1
3211.976	30	4	I	.....	3250.04	1	20hl	II	.....
3212.64	4	.....	I	.....	3252.144	9	.....	I	.....
3213.708	70	5	I	3	3253.695	400	1000	II	5
3214.230	20	1	I	.....	3254.854	40	5	I	.....
3215.269	2	7hl	II	.....	3255.28	200	500	II	5
3216.01	1	.....	I	.....	3256.16	10	10hl	II	.....

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
3256.37	.....	4h	II	.....	3291.043	150	100	I	3
3256.66	1	.....	I	.....	3291.340	30	.....	I	.....
3256.87	1	5Hl	II	.....	3291.600	50	3	I	.....
3256.96	4	.....	I	.....	3292.095	4	.....	I	.....
3258.50	2	.....	I	.....	3292.312	10	.....	I	.....
3258.57	3	.....	I	.....	3293.116	60	4	I	.....
3258.84	1	.....	I	.....	3293.457	10	.....	I	.....
3258.88	2	.....	I	.....	3293.998	3	.....	I	.....
3259.35	5	60Hl	II	.....	3294.649	2	200	II	4
3259.97	1	.....	I	.....	3294.745	15	.....	I	.....
3260.12	1	.....	I	.....	3295.585	30	1	I	.....
3260.63	1	.....	I	.....	3296.027	20	1	I	.....
3260.947	2	.....	I	.....	3296.445	4	.....	I	.....
3261.39	3	.....	I	.....	3297.673	10	.....	I	.....
3261.52	2	.....	I	.....	3298.350	40	2	I	.....
3261.898	50	10	I	.....	3298.495	10	.....	I	.....
3262.469	100	15	I	3	3298.934	80	6	I	.....
3263.92	1	1hl	II	.....	3299.662	40	.....	I	.....
3264.485	15	.....	I	.....	3300.11	.....	6h	III	.....
3264.903	7	.....	I	.....	3300.290	10	.....	I	.....
3265.281	80	10	I	2	3301.06	1	.....	I	.....
3265.570	15	.....	I	.....	3302.164	20	2	I	.....
3265.97	1	.....	I	.....	3302.26	2	.....	I	.....
3266.525	2	30h	II	5	3302.94	7	.....	I	.....
3267.000	70	10	I	1	3303.317	7	.....	I	.....
3267.165	80	10	I	1	3303.871	30	2	I	.....
3268.25	3	.....	I	.....	3304.07	2	5Hl	II	.....
3268.32	1	.....	I	.....	3304.42	1	.....	I	.....
3268.653	7	.....	I	.....	3304.60	3	.....	I	.....
3269.65	1	.....	I	.....	3306.110	300	30	I	3
3270.58	2	7	II	.....	3306.374	60	2	I	.....
3272.03	1	.....	I	.....	3307.36	1	.....	I	.....
3272.930	30	.....	I	7	3308.390	10	.....	I	.....
3273.646	40	300	II	6	3309.193	100	10	I	7
3273.94	3	20	II	.....	3309.54	9	.....	I	.....
3275.065	8	.....	I	.....	3310.274	300	70	I	1
3275.44	15	.....	I	.....	3310.825	5	200	II	6
3276.431	30	1	I	.....	3311.115	1	10h	II	.....
3277.83	4	.....	I	.....	3312.06	1	.....	I	.....
3278.080	40	1	I	.....	3312.869	600	100	I	3
3279.002	10	.....	I	.....	3313.98	4	.....	I	.....
3279.67	.....	200H	III	.....	3314.020	3	60h	II	.....
3279.971	100	500	II	6	3314.11	8	.....	I	.....
3282.977	100	40	I	.....	3314.77	2	.....	I	.....
3283.382	20	200	II	5	3316.167	100	10	I	.....
3284.81	3	.....	I	.....	3316.54	1	7h	II	.....
3285.213	8	.....	I	.....	3317.252	5	30	II	5
3285.472	6	.....	I	.....	3317.985	100	400	II	6
3285.644	30	.....	I	.....	3318.281	40	2	I	.....
3286.26	1	.....	I	.....	3318.727	4	10	II	.....
3286.50	1	.....	I	.....	3319.257	10	.....	I	.....
3286.88	4	5h	II	.....	3319.43	8	.....	I	.....
3287.286	70	10	I	2	3320.06	3	.....	I	.....
3288.31	2	.....	I	.....	3320.228	3	.....	I	.....
3288.46	1	5h	II	.....	3320.97	6	.....	I	.....
3288.722	15	.....	I	.....	3321.146	2	.....	I	.....
3288.78	.....	9Hl	III	.....	3321.274	4	.....	I	.....
3289.720	10	70	II	6	3321.50	3	.....	I	.....
3290.05	1	.....	I	.....	3321.946	15	1	I	.....
3290.25	2	.....	I	.....	3322.48	1	.....	I	.....

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity: Tube	Intensity: Spark	Spectrum	Zeeman type
A				
3322.719	5	------	I	-----
3323.03	3	------	I	-----
3323.09	2	------	I	-----
3323.324	20	500	II	5
3323.77	3	------	I	-----
3324.168	10	100	II	5
3324.395	5	------	I	-----
3326.063	4	------	I	-----
3326.315	7	------	I	-----
3326.92	3	------	I	-----
3327.46	2	------	I	-----
3327.705	15	------	I	-----
3328.211	40	300	II	6
3328.42	10	------	I	-----
3328.73	2	------	I	-----
3329.40	10	------	I	-----
3330.183	20	1	I	-----
3331.44	10	------	I	-----
3331.857	50	4	I	-----
3332.737	600	100	I	2
3333.47	1	70hl	II	-----
3333.906	20	------	I	-----
3334.388	10	------	I	-----
3335.108	30	1	I	-----
3336.08	20	------	I	-----
3336.39	1	------	I	-----
3336.77	2	10Hl	II	-----
3337.73	5	------	I	-----
3337.995	7	------	I	-----
3338.594	9	------	I	-----
3339.02	6	------	I	-----
3339.34	7	------	I	-----
3340.13	1	------	I	-----
3340.459	9	------	I	-----
3340.98	1	------	I	-----
3341.05	6	------	I	-----
3341.29	1	------	I	-----
3341.870	4	------	I	-----
3342.73	5	------	I	-----
3344.305	20	1	I	-----
3345.01	1	------	I	-----
3345.10	6	------	I	-----
3345.334	1	------	I	-----
3346.05	5	------	I	-----
3346.95	4	------	I	-----
3348.38	5	------	I	-----
3348.710	7	------	I	-----
3349.167	4	100	II	6
3349.24	20	------	I	-----
3350.33	40	------	I	-----
3352.063	400	1000	II	7
3353.028	50	4	I	-----
3353.50	7	------	I	-----
3354.70	7	------	I	-----
3355.01	20	------	I	-----
3356.012	10	50	II	-----
3356.34	4	------	I	-----
3356.788	80	10	I	-----
3358.187	20	------	I	-----
3358.288	30	300	II	5
3358.906	50	10	I	-----
3358.965	100	20	I	7
3360.060	200	30	I	3
3361.22	6	------	I	-----
3361.44	3	10Hl	II	-----
3362.52	1	------	I	-----
3363.44	2	------	I	-----
3363.74	15	------	I	-----
3364.157	10	------	I	-----
3364.600	20	------	I	-----
3365.20	1	------	I	-----
3365.452	2	------	I	-----
3365.778	10	100Hl	II	7
3366.681	100	20	I	3
3367.078	4	10	II	-----
3368.50	3	------	I	-----
3368.850	4	------	I	-----
3370.677	10	200Hl	II	-----
3371.04	20	------	I	-----
3371.46	10	------	I	-----
3371.92	7	------	I	-----
3372.201	60	5	I	2
3372.78	10	1	I	-----
3374.974	10	------	I	-----
3375.265	15	------	I	-----
3375.548	2	------	I	-----
3375.844	7	------	I	-----
3376.055	15	------	I	-----
3376.517	9	------	I	-----
3376.669	12	80	II	6
3376.90	2	------	I	-----
3377.02	5	------	I	-----
3378.876	60	6	I	-----
3378.932	150	10	I	-----
3379.712	7	------	I	-----
3380.062	15	------	I	-----
3380.79	1	4hl	II	-----
3381.377	40	3	I	-----
3382.334	30	1	I	-----
3382.79	1	------	I	-----
3383.040	2	------	I	-----
3383.80	3	------	I	-----
3384.14	40	700	II	-----
3384.694	70	500	II	5
3385.196	10	150h	II	-----
3386.214	150	20	I	3
3386.907	6	------	I	-----
3388.534	3	------	I	-----
3389.833	200	2000	II	5
3390.465	50	5	I	-----
3391.43	1	------	I	-----
3391.97	7	20	II	-----
3392.450	30	1	I	-----
3392.815	150	40	I	3
3393.900	15	------	I	-----
3394.162	10	------	I	-----
3394.575	200	1000	II	6
3394.980	150	2000	II	6
3395.888	100	4	I	-----
3396.65	4	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
3397. 257	200	20	I	3
3397. 602	100	20	I	7
3398. 54	3	.....	I	.....
3399. 793	1000	5000	II	5
3400. 218	200	20	I	.....
3401. 73	3	2	I	.....
3402. 512	200	20	I	2
3405. 304	6	.....	I	.....
3405. 89	4	.....	I	.....
3407. 140	50	10	I	3
3407. 750	40	700	II	5
3407. 928	20	.....	I	.....
3408. 63	7	.....	I	.....
3408. 679	8	.....	I	.....
3409. 546	20	1	I	.....
3409. 724	10	.....	I	.....
3410. 157	150	2000	II	6
3410. 892	7	.....	I	.....
3411. 253	10	.....	I	.....
3411. 734	5	.....	I	.....
3412. 016	20	.....	I	.....
3412. 374	100	10	I	2
3412. 687	8	.....	I	.....
3413. 732	30	400h	II	5
3414. 313	7	.....	I	.....
3414. 543	2	.....	I	.....
3415. 20	2	9Hl	II	.....
3416. 04	3	15Hl	II	.....
3416. 52	1	.....	I	.....
3416. 82	3	.....	I	.....
3417. 34	300	30	I	2
3419. 171	500	90	I	1
3419. 80	5	.....	I	.....
3419. 87	2	.....	I	.....
3420. 00	1	.....	I	.....
3420. 775	20	.....	I	.....
3421. 435	40	100	II	5
3422. 542	15	.....	I	.....
3423. 08	7	.....	I	.....
3423. 500	20	.....	I	.....
3423. 656	8	.....	I	.....
3426. 478	30	1	I	.....
3427. 430	150	20	I	.....
3428. 363	200	500	II	1
3431. 189	10	.....	I	5
3431. 79	3	.....	I	.....
3432. 28	2	.....	I	.....
3432. 577	9	.....	I	.....
3434. 639	50	4	I	.....
3434. 969	15	1	I	.....
3435. 277	15	.....	I	.....
3435. 58	1	8hl	II	.....
3436. 438	40	2	I	.....
3436. 81	9	.....	I	.....
3437. 15	1	.....	I	.....
3437. 30	.....	10H	III	.....
3438. 29	.....	5H	III	.....
3438. 428	300	30	I	7
3439. 669	20	1	I	
3440. 07	1	10Hl	II	

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
3440. 860	100	6	I	
3441. 835	150	8	I	.....
3443. 412	2	10h	II	2
3444. 140	7	.....	I	.....
3445. 068	10	.....	I	.....
3446. 481	10	10h	II	.....
3447. 446	30	2	I	.....
3448. 284	100	8	I	.....
3448. 969	50	3	I	7
3449. 82	6	.....	I	.....
3450. 33	2	10Hl	II	.....
3450. 54	1	.....	I	.....
3451. 522	20	1	I	.....
3451. 64	1	7Hl	II	.....
3452. 304	70	10	I	.....
3452. 576	15	.....	I	2
3452. 619	10	.....	I	.....
3453. 136	40	3	I	.....
3453. 525	40	3	I	.....
3455. 858	10	.....	I	.....
3455. 998	10	.....	I	.....
3456. 39	2	.....	I	.....
3456. 831	30	.....	I	.....
3457. 559	1	1h	II	.....
3458. 18	1	.....	I	.....
3458. 69	8	.....	I	.....
3459. 98	2	.....	I	.....
3460. 720	20	.....	I	.....
3461. 250	6	.....	I	.....
3461. 33	5	.....	I	.....
3461. 77	3	.....	I	.....
3462. 12	5	.....	I	.....
3462. 646	150	300	II	5
3464. 12	2	.....	I	.....
3464. 720	50	2	I	.....
3465. 120	30	1	I	.....
3465. 93	5	40	II	6
3467. 410	20	1	I	.....
3467. 569	150	15	I	2
3468. 810	3	15	II	.....
3468. 99	5	.....	I	.....
3469. 260	5	20	II	.....
3469. 91	1	.....	I	.....
3470. 300	7	.....	I	.....
3470. 800	15	.....	I	.....
3470. 910	10	.....	I	.....
3472. 410	800	100	I	1
3473. 982	30	.....	I	.....
3475. 16	60	3	I	.....
3475. 483	30	2	I	.....
3475. 59	6	20Hl	II	.....
3476. 450	20	.....	I	.....
3476. 573	40	.....	I	.....
3477. 96	2	10hl	II	.....
3478. 978	100	1000	II	6
3479. 284	250	1500	II	7
3481. 05	7	.....	I	.....
3481. 410	15	.....	I	.....
3481. 895	70	3	I	.....
3483. 111	50	2	I	.....

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
3484. 14	2	8Hl	II	.....	3532. 500	5	.....	I	.....
3484. 718	100	6	I	.....	3532. 978	40	2	I	.....
3485. 167	20	50	II	5	3534. 041	4	.....	I	.....
3487. 573	20	300	II	4	3534. 498	30	2	I	.....
3487. 886	10	.....	I	.....	3535. 549	500	2000	II	7
3488. 018	30	2	I	.....	3536. 630	400	50	I	3
3488. 324	10	.....	I	.....	3537. 75	2	8Hl	II	.....
3489. 29	2	.....	I	.....	3540. 166	10	.....	I	.....
3489. 628	10	.....	I	.....	3541. 33	3	.....	I	.....
3489. 918	6	.....	I	.....	3541. 45	1	.....	I	.....
3490. 540	70	2	I	.....	3541. 65	2	.....	I	.....
3491. 587	60	1	I	.....	3542. 503	60	4	I	.....
3492. 012	6	.....	I	.....	3543. 56	10	.....	I	.....
3492. 242	10	.....	I	.....	3543. 828	3	.....	I	.....
3493. 20	1	.....	I	.....	3544. 760	5	40	II	
3493. 551	15	.....	I	.....	3545. 017	20	1	I	.....
3493. 726	7	.....	I	.....	3545. 937	50	2	I	.....
3494. 174	60	3	I	.....	3547. 865	30	1	I	.....
3494. 99	20	.....	I	.....	3548. 816	300	30	I	.....
3495. 750	150	700	II	5	3549. 218	10	.....	I	.....
3495. 934	50	400	II	5	3549. 632	20	.....	I	.....
3497. 168	400	60	I	.....	3550. 283	2	10	II	.....
3497. 498	1500	150	I	2	3550. 696	30	1	I	.....
3498. 988	100	10	I	1	3551. 743	20	.....	I	.....
3499. 96	2	3h	II	.....	2552. 706	400	1000	II	6
3500. 575	6	.....	I	.....	3553. 44	5	.....	I	.....
3502. 831	2	5h	II	.....	3554. 015	150	20	I	.....
3505. 227	2000	6000	II	4	3555. 004	30	1	I	.....
3506. 872	10	.....	I	.....	3556. 05	5	.....	I	.....
3508. 248	30	1	I	.....	3556. 995	20	.....	I	.....
3509. 077	30	1	I	.....	3557. 083	10	.....	I	.....
3510. 418	20	.....	I	.....	3558. 470	100	10	I	.....
3511. 039	5	10Hl	II	.....	3559. 83	2	4h	II	.....
3511. 297	100	5	I	.....	3561. 654	1500	3000	II	6
3511. 847	30	200	II	5	3563. 253	7	.....	I	.....
3513. 271	300	30	I	3	3563. 634	30	3	I	7
3513. 535	40	1	I	.....	3564. 307	200	30	I	7
3515. 06	2	.....	I	.....	3564. 652	40	2	I	.....
3515. 606	10	20	II	.....	3564. 868	10	.....	I	.....
3516. 105	4	.....	I	.....	3566. 59	1	.....	I	.....
3516. 817	80	4	I		3567. 360	600	50	I	3
3517. 732	60	3	I	.....	3569. 036	1000	3000	II	4
3518. 360	10	40	II	.....	3570. 971	4	.....	I	.....
3518. 742	100	400	II	6	3572. 016	20	2	I	.....
3519. 62	10	.....	I	.....	3573. 074	8	.....	I	.....
3520. 270	10	.....	I	.....	3574. 39	1	.....	I	.....
3521. 560	100	10	I	.....	3574. 785	10	1	I	.....
3522. 223	30	.....	I	.....	3574. 813	20	2	I	.....
3523. 025	1000	100	I	2	3575. 44	1	.....	I	.....
3523. 50	10	40Hl	II	.....	3576. 43	1	.....	I	.....
3525. 547	90	5	I	.....	3577. 546	7	.....	I	.....
3526. 651	20	1	I	.....	3577. 96	1	.....	I	.....
3526. 872	80	4	I	.....	3579. 899	150	15	I	.....
3528. 217	30	.....	I	.....	3580. 466	10	100	II	4
3529. 358	10	.....	I	.....	3581. 564	15	.....	I	.....
3529. 694	3	.....	I	.....	3582. 006	4	.....	I	.....
3530. 870	80	4	I	.....	3583. 267	100	10	I	3
3530. 947	50	2	I	.....	3583. 646	3	10Hl	II	.....
3531. 224	200	15	I	1	3584. 215	3	.....	I	.....
3531. 83	3	.....	I	.....	3585. 073	6	.....	I	.....

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
3586. 383	15	1	I		3627. 850	70	10	I	1
3587. 142	20	4	I		3628. 116	10		I	
3587. 23	5		I		3628. 96	2		I	
3587. 884	2		I		3630. 872	700	100	I	1
3588. 258	7		I		3632. 02	2	10Hl	II	
3588. 849	10	1	I		3632. 323	4	20h	II	
3589. 557	2		I		3632. 694	40	5	I	
3589. 684	3		I		3633. 181	10	90	II	5
3590. 349	9		I		3633. 513	5		I	
3590. 86	1		I		3634. 12	4		I	
3591. 113	2	20	II		3634. 144	5		I	
3592. 12	1		I		3635. 254	20	2	I	
3592. 67	1		I		3635. 425	150	10	I	2
3593. 55	5		I		3636. 31	1		I	
3593. 608	30	2	I		3637. 06	1		I	
3594. 434	5	30	II	5	3637. 594	90	7	I	3
3595. 06	1		I		3638. 728	15		I	
3595. 888	2		I		3638. 885	1		I	
3596. 11	1		I		3639. 95	1		I	
3596. 27	3		I		3639. 97	1		I	
3597. 403	30	300	II	6	3641. 80	1		I	
3597. 501	60	10	I	3	3642. 552	5	20hl	II	
3598. 510	6		I		3644. 357	1000	3000	II	7
3598. 614	7		I		3645. 351	6		I	
3599. 108	10	100	II	6	3646. 63	1		I	
3599. 284	3	30	II		3647. 467	1	15	II	
3599. 867	200	60	I	1	3647. 54	5		I	
3600. 04	2	70hl	II	6	3648. 348	5	100	II	5
3601. 68	1		I		3649. 106	700	60	I	1
3602. 202	3		I		3650. 535	100	10	I	
3602. 42	1		I		3651. 838	400	40	I	3
3602. 914	2		I		3652. 902	1	7	II	
3603. 626	40	4	I		3653. 34	1		I	
3603. 994	15		I		3653. 46	1		I	
3605. 26	1		I		3654. 57	1		I	
3605. 322	2		I		3654. 756	5		I	
3605. 50	1		I		3655. 652	30	2	I	
3606. 231	2		I		3656. 406	2		I	
3606. 784	5		I		3656. 60	2	15Hl	II	
3607. 844	3		I		3657. 428	2		I	
3608. 646	8		I		3657. 776	15		I	
3609. 116	50	8	I		3658. 22	1		I	
3610. 851	8		I		3658. 49	6		I	
3611. 42	2		I		3658. 50	2		I	
3611. 462	4		I		3659. 031	10	100	II	4
3612. 127	10		I		3660. 36	1		I	
3612. 479	30	4	I		3661. 046	30	400	II	5
3615. 034	300	30	I	2	3661. 385	30	2	I	
3616. 892	2000	200	I	3	3661. 711	3		I	
3617. 699	50	8	I		3661. 734	3	30	II	
3618. 684	20		I		3662. 92	1	3h	II	
3618. 732	30	2	I		3663. 36	10		I	
3620. 041	100	10	I	7	3664. 020	1		I	
3620. 432	6		I		3664. 57	80	8	I	
3621. 79	1		I		3665. 343	200	1000	II	4
3622. 311	4		I		3666. 279	20		I	
3622. 450	15	100	II	4	3666. 597	1	20hl	II	
3623. 994	70	300	II	4	3666. 818	5	50	II	4
3625. 42	1		I		3667. 24	5		I	
3625. 93	3		I		3668. 19	100	10	I	1

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
3668. 59	2	------	I	-----
3669. 49	15	1	I	-----
3672. 13	1	10Hl	II	-----
3672. 304	300	30	I	7
3673. 06	3	------	I	-----
3674. 07	2	------	I	-----
3675. 742	400	150	I	1
3676. 34	9	------	I	-----
3676. 716	3	------	I	-----
3677. 50	1	------	I	-----
3677. 681	3	------	I	-----
3678. 028	2	60hl	II	5
3681. 384	20	100	II	4
3682. 247	3000	200	I	3
3683. 57	5	------	I	-----
3685. 352	3	------	I	-----
3685. 94	4	------	I	-----
3687. 42	9	------	I	-----
3687. 76	2	------	I	-----
3687. 84	2	------	I	-----
3688. 756	9	------	I	-----
3690. 10	3	------	I	-----
3691. 185	20	2	I	-----
3691. 45	2	------	I	-----
3692. 770	4	------	I	-----
3693. 156	10	------	I	-----
3693. 60	20	3	I	-----
3694. 16	40	4	I	-----
3695. 72	2	------	I	-----
3696. 524	400	40	I	1
3697. 08	50	4	I	-----
3697. 61	4	------	I	-----
3698. 392	30	400	II	4
3698. 83	3	------	I	-----
3699. 55	------	10	II	-----
3699. 57	5	------	I	-----
3699. 73	70	1000	II	7
3701. 158	80	2000	II	4
3701. 83	15	------	I	-----
3702. 31	3	60hl	II	7
3702. 93	1	------	I	-----
3703. 154	2	------	I	-----
3703. 816	10	------	I	-----
3704. 067	15	------	I	-----
3704. 351	6	------	I	-----
3704. 657	2	30hl	II	-----
3704. 938	40	3	I	-----
3705. 404	20	500	II	6
3707. 02	1	------	I	-----
3707. 374	70	7	I	1
3707. 92	1	------	I	-----
3708. 500	3	------	I	-----
3708. 85	1	------	I	-----
3709. 044	4	------	I	-----
3711. 142	4	50hl	II	-----
3711. 692	3	------	I	-----
3711. 83	1	------	I	-----
3712. 22	4	------	I	-----
3712. 52	1	------	I	-----
3712. 642	7	------	I	-----
A				
3716. 054	30	2	I	-----
3717. 144	80	7	I	-----
3717. 802	1000	100	I	7
3718. 781	2	30	II	-----
3719. 278	300	3000	II	4
3721. 500	80	7	I	-----
3722. 66	1	20	II	6
3722. 904	4	------	I	-----
3723. 38	5	------	I	-----
3724. 444	2	------	I	-----
3725. 68	1	------	I	-----
3726. 485	150	15	I	2
3727. 092	3	------	I	-----
3728. 179	2	------	I	-----
3728. 378	3	------	I	-----
3729. 093	150	15	I	7
3730. 760	20	1	I	-----
3732. 99	2	------	I	-----
3733. 786	1000	100	I	1
3735. 364	5	------	I	-----
3736. 303	20	1	I	-----
3737. 866	30	1000	II	7
3739. 030	150	10	I	3
3739. 68	2	------	I	-----
3739. 835	2	7Hl	II	-----
3741. 12	2	------	I	-----
3741. 396	6	------	I	-----
3741. 94	------	100H	III	-----
3744. 002	30	2	I	-----
3744. 958	20	500	II	6
3745. 765	2	7hl	II	-----
3746. 810	400	60	I	1
3747. 481	20	200	II	7
3748. 554	5	------	I	-----
3748. 672	3	------	I	-----
3748. 71	1	------	I	-----
3749. 829	8	------	I	-----
3750. 55	1	------	I	-----
3751. 778	10	------	I	-----
3751. 824	15	1	I	-----
3752. 784	20	2	I	-----
3753. 225	100	20	I	3
3754. 26	1	------	I	-----
3755. 024	5	------	I	-----
3755. 620	4	------	I	-----
3755. 71	2	------	I	-----
3755. 99	1	------	I	-----
3756. 17	1	------	I	-----
3756. 645	2	------	I	-----
3756. 850	3	------	I	-----
3756. 98	1	------	I	-----
3757. 554	20	1	I	-----
3758. 020	7	100	II	4
3760. 75	1	------	I	-----
3761. 79	2	------	I	-----
3762. 500	30	1000	II	4
3763. 232	20	2	I	-----
3763. 524	1	------	I	-----
3763. 943	4	------	I	-----
3764. 528	90	8	I	7

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
3765. 046	100	9	I	7	3811. 781	400	40	I	3
3765. 558	100	10	I	1	3813. 34	1	------	I	-----
3766. 917	20	2000	II	4	3813. 69	1	------	I	-----
3768. 254	200	10	I	3	3813. 848	9	------	I	-----
3770. 32	1	------	I	-----	3813. 972	5	------	I	-----
3770. 603	3	60hl	II	6	3814. 992	4	------	I	-----
3771. 350	20	200	II	6	3815. 542	30	2	I	-----
3771. 98	7	------	I	-----	3816. 069	60	6	I	-----
3772. 824	2	15hl	II	-----	3816. 59	1	------	I	-----
3773. 122	50	4	I	-----	3817. 196	30	400	II	4
3776. 78	5	------	I	-----	3818. 112	15	------	I	-----
3777. 10	5	------	I	-----	3818. 834	2	------	I	-----
3777. 658	2000	200	I	1	3819. 348	50	7	I	-----
3779. 87	5	------	I	-----	3819. 882	1	10hl	II	-----
3780. 092	20	100	II	6	3819. 90	3	------	I	-----
3780. 620	3	------	I	-----	3820. 728	1000	100	I	3
3781. 016	2	------	I	-----	3822. 64	4	------	I	-----
3781. 46	5	------	I	-----	3822. 819	6	------	I	-----
3781. 550	5	------	I	-----	3823. 510	5	100hl	II	6
3782. 437	60	5	I	-----	3823. 838	5	------	I	-----
3782. 782	15	200	II	5	3824. 58	6	------	I	-----
3785. 46	3000	250	I	1	3824. 961	50	4	I	-----
3787. 375	50	4	I	1	3826. 46	3	------	I	-----
3787. 980	10	------	I	-----	3828. 506	30	1	I	-----
3788. 110	5	------	I	-----	3829. 686	100	20	I	3
3788. 368	6	------	I	-----	3830. 018	200	50	I	2
3788. 520	15	------	I	-----	3830. 658	15	1	I	-----
3788. 837	10	------	I	-----	3831. 120	40	3	I	-----
3789. 27	7	------	I	-----	3831. 94	1	------	I	-----
3790. 718	2	------	I	-----	3833. 502	40	3	I	-----
3790. 87	1	------	I	-----	3833. 667	60	5	I	1
3791. 14	3	------	I	-----	3834. 23	3	------	I	-----
3791. 398	3	------	I	-----	3834. 423	4	------	I	-----
3791. 592	6	------	I	-----	3834. 484	7	------	I	-----
3791. 907	4	------	I	-----	3834. 703	1	7hl	II	-----
3791. 94	4	------	I	-----	3837. 196	4	------	I	-----
3792. 56	1	------	I	-----	3838. 355	5	50hl	II	4
3793. 384	500	1000	II	6	3839. 55	4	------	I	-----
3794. 66	2	------	I	-----	3841. 107	8	------	I	-----
3794. 964	15	1	I	-----	3842. 782	9	------	I	-----
3795. 366	10	------	I	-----	3843. 214	5	------	I	-----
3795. 704	7	------	I	-----	3843. 402	2	------	I	-----
3796. 29	1	6hl	II	-----	3844. 11	1	------	I	-----
3796. 66	1	------	I	-----	3845. 962	8	------	I	-----
3797. 935	20	200	II	7?	3846. 521	7	------	I	-----
3798. 68	150	15	I	-----	3849. 19	1000	70	I	3
3799. 230	4	------	I	-----	3849. 517	40	1000	II	7
3799. 49	5	50	II	-----	3850. 364	50	4	I	-----
3799. 83	10	------	I	-----	3851. 676	20	1	I	-----
3800. 38	1000	100	I	2	3852. 52	1	------	I	-----
3800. 452	300	50	I	3	3852. 716	20	1	I	-----
3801. 92	1	------	I	-----	3852. 978	2	------	I	-----
3802. 652	15	------	I	-----	3854. 354	40	3	I	-----
3804. 198	50	4	I	-----	3854. 638	5	------	I	-----
3804. 533	100	10	I	-----	3854. 95	1	------	I	-----
3805. 44	1	------	I	-----	3858. 31	800	80	I	1
3806. 065	30	1000	II	4	3860. 910	200	20	I	1
3809. 882	3	------	I	-----	3861. 885	7	------	I	-----
3810. 575	10	200	II	4	3863. 436	20	2	I	-----
3810. 61	7	------	I	-----	3863. 655	2	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity: Tube	Intensity: Spark	Spectrum	Zeeman type
A				
3864. 10	1	------	I	-----
3864. 730	30	800	II	4
3865. 684	10	------	I	-----
3865. 979	10	------	I	-----
3866. 16	1	------	I	-----
3867. 310	30	400	II	4
3867. 95	1	------	I	-----
3870. 962	50	3	I	-----
3871. 605	2	------	I	-----
3872. 546	40	300	II	5
3873. 74	1	------	I	-----
3874. 08	2	------	I	-----
3874. 99	1	------	I	-----
3875. 77	1	------	I	-----
3876. 280	30	1	I	-----
3877. 095	40	600	II	4
3878. 947	20	1	I	-----
3879. 216	60	5	I	-----
3880. 814	300	600	II	5
3882. 216	6	60	II	-----
3882. 527	100	10	I	-----
3883. 762	100	400	II	4
3885. 35	1	------	I	-----
3885. 420	10	------	I	-----
3885. 624	2	------	I	-----
3885. 804	30	2	I	-----
3886. 42	------	5H	II	-----
3886. 767	2	7h	II	-----
3889. 228	150	20	I	1
3889. 362	200	30	I	2
3890. 683	15	------	I	-----
3891. 470	10	------	I	-----
3891. 90	3	------	I	-----
3892. 03	1	------	I	-----
3892. 472	60	4	I	-----
3893. 118	10	------	I	-----
3893. 26	1	------	I	-----
3893. 594	10	------	I	-----
3894. 08	7	------	I	-----
3899. 937	1000	80	I	3
3900. 619	20	500	II	7
3901. 44	20	1	I	-----
3902. 937	90	8	I	7
3903. 20	10	------	I	-----
3903. 824	6	------	I	-----
3905. 520	20	------	I	-----
3905. 79	3	------	I	-----
3906. 107	1	------	I	-----
3906. 888	80	5	I	1
3908. 800	30	------	I	-----
3909. 185	100	10	I	-----
3909. 67	2	------	I	-----
3910. 29	10	------	I	-----
3910. 876	4	------	I	-----
3911. 748	15	------	I	-----
3912. 21	1	------	I	-----
3912. 436	7	------	I	-----
3912. 67	2	------	I	-----
3913. 89	1	------	I	-----
3913. 93	2	------	I	-----
3914. 060	1	------	I	-----
3915. 53	1	------	I	-----
3916. 074	20	1	I	-----
3916. 368	30	2	I	-----
3917. 25	1	------	I	-----
3917. 442	30	200	II	6
3918. 096	300	600	II	4
3919. 417	3	------	I	-----
3919. 740	9	------	I	-----
3920. 137	3	------	I	-----
3922. 312	4	------	I	-----
3922. 784	8	------	I	-----
3923. 714	20	1	I	-----
3923. 898	150	400	II	4
3926. 434	100	8	I	2
3927. 108	10	------	I	-----
3927. 585	100	15	I	3
3928. 044	1	7hl	II	-----
3928. 722	10	------	I	-----
3929. 49	2	20hl	II	7
3930. 895	------	5hl	II	-----
3931. 38	700	70	I	7
3931. 761	20	2	I	-----
3931. 94	1	10hl	II	-----
3932. 386	20	70h	II	4
3933. 166	2	15h	II	-----
3933. 653	40	100h	II	5
3935. 11	1	------	I	-----
3935. 634	30	200	II	5
3937. 28	1	------	I	-----
3938. 20	1	------	I	-----
3938. 48	10	1	I	-----
3939. 042	100	5	I	3
3939. 604	------	6hl	II	-----
3940, 346	20	1	I	-----
3941. 92	15	1	I	-----
3942. 73	20	1	I	-----
3943. 06	40	3	I	-----
3943. 60	3	------	I	-----
3944. 16	1	------	I	-----
3944. 59	3	------	I	-----
3945. 33	7	100hl	II	6
3945. 87	2	------	I	-----
3945. 96	5	80hl	II	5
3947. 977	9	------	I	-----
3948. 299	4	------	I	-----
3948. 423	2	------	I	-----
3949. 497	20	2	I	-----
3949. 80	7	------	I	-----
3950. 78	50	6	I	-----
3951. 18	8	------	I	-----
3951. 822	1000	100	I	3
3955. 80	3	------	I	-----
3956. 080	5	------	I	-----
3956. 39	1	------	I	-----
3957. 026	40	2	I	-----
3957. 440	10	------	I	-----
3957. 73	9	------	I	-----
3958. 982	15	------	I	-----
3959. 702	20	1	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
3960. 54	1	------	I	-----
3961. 68	1	------	I	-----
3962. 04	1	------	I	-----
3962. 764	3	------	I	-----
3963. 472	4	------	I	-----
3963. 944	1	------	I	-----
3964. 956	20	300	II	5
3966. 162	10	------	I	-----
3966. 938	3	------	I	-----
3967. 254	30	2	I	-----
3968. 008	400	20	I	-----
3968. 985	10	------	I	-----
3969. 79	2	------	I	-----
3972. 228	20	1	I	-----
3972. 642	3	------	I	-----
3973. 477	600	20	I	2
3975. 132	3	30hl	II	5
3975. 624	2	------	I	-----
3977. 383	40	2	I	-----
3979. 370	20	500	II	4
3981. 148	10	1	I	-----
3981. 698	80	3	I	-----
3983. 87	3	------	I	-----
3984. 02	20	100	II	6
3984. 83	7	200hl	II	5
3985. 32	1	------	I	-----
3985. 57	3	------	I	-----
3985. 67	6	------	I	-----
3987. 270	20	------	I	-----
3988. 128	4	------	I	-----
3988. 70	2	------	I	-----
3989. 28	1	------	I	-----
3989. 37	1	------	I	-----
3989. 48	2	------	I	-----
3989. 61	3	------	I	-----
3990. 00	1	------	I	-----
3990. 524	2	------	I	-----
3991. 25	4	------	I	-----
3991. 77	1	------	I	-----
3991. 82	2	------	I	-----
3992. 75	40	2	I	-----
3993. 35	3	------	I	-----
3995. 99	1	2	II	-----
3996. 53	1	------	I	-----
3996. 79	15	60	II	4
3997. 09	30	------	I	-----
3997. 807	20	------	I	-----
3998. 001	15	------	I	-----
3998. 15	2	------	I	-----
3998. 38	5	20hl	II	-----
3998. 54	7	40	II	6
3999. 79	1	------	I	-----
4001. 53	40	2	I	-----
4003. 432	3	------	I	-----
4003. 715	10	1	I	-----
4004. 385	40	2	I	-----
4004. 679	15	1	I	-----
4005. 490	3	------	I	-----
4006. 480	2	------	I	-----
4006. 90	1	------	I	-----
A				
4007. 337	8	80	II	5
4007. 59	1	------	I	-----
4008. 452	15	60	II	6
4008. 95	1	------	I	-----
4009. 862	20	------	I	-----
4011. 503	100	4	I	-----
4012. 24	1	------	I	-----
4013. 259	7	------	I	-----
4013. 58	1	------	I	-----
4015. 672	40	2	I	-----
4016. 99	1	------	I	-----
4017. 685	3	------	I	-----
4018. 912	9	------	I	-----
4019. 274	1	------	I	-----
4019. 68	1	------	I	-----
4020. 247	15	30	II	6
4021. 593	7	------	I	-----
4022. 151	3h	------	I	-----
4022. 830	40	2	I	-----
4023. 976	1	------	I	-----
4024. 918	20	------	I	-----
4026. 22	1	------	I	-----
4026. 29	2	------	I	-----
4026. 470	2	------	I	-----
4027. 72	1	------	I	-----
4029. 158	30	70	II	5
4030. 03	1	------	I	-----
4030. 68	1	------	I	-----
4031. 924	20	2	I	-----
4032. 266	300	15	I	2
4033. 861	10	40	II	5
4034. 48	4	------	I	-----
4035. 65	2	------	I	-----
4035. 76	1	------	I	-----
4035. 888	3	------	I	-----
4036. 15	1	3h	II	-----
4037. 224	5	------	I	-----
4037. 64	1	------	I	-----
4038. 379	30	2	I	-----
4038. 646	20	------	I	-----
4039. 56	1	------	I	-----
4040. 35	1	------	I	-----
4041. 63	1	------	I	-----
4041. 768	40	2	I	-----
4043. 571	2	------	I	-----
4044. 370	80	8	I	2
4045. 198	6	------	I	-----
4045. 444	5	------	I	-----
4046. 041	3	------	I	-----
4046. 64	1	------	I	-----
4047. 600	20	1	I	-----
4047. 790	15	------	I	-----
4047. 950	10	300hl	II	5
4048. 443	2	20hl	II	-----
4048. 664	40	2	I	-----
4049. 446	10	100hl	II	6
4049. 702	30	2	I	-----
4050. 670	7	60	II	5
4050. 883	100	5	I	2
4053. 246	40	4	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
4054. 686	20	2	I	-----	4105. 10	2	------	I	-----
4055. 70	1	------	I	-----	4105. 58	8	------	I	-----
4055. 928	6	------	I	-----	4105. 63	8	------	I	-----
4057. 439	80	6	I	3	4105. 81	15	1	I	-----
4058. 124	2	------	I	-----	4106. 553	200	15	I	2
4058. 626	1	------	I	-----	4107. 09	4	------	I	-----
4060. 085	4	------	I	-----	4107. 21	------	6H	II	-----
4062. 84	400	60	I	3	4107. 76	1	------	I	-----
4063. 754	5	------	I	-----	4108. 73	------	6h	II	-----
4064. 880	20	1	I	-----	4108. 821	7	------	I	-----
4066. 21	200	30	I	3	4109. 44	1	------	I	-----
4067. 830	100	10	I	1	4109. 52	1	------	I	-----
4068. 256	70	3	I	-----	4110. 412	2	------	I	-----
4070. 168	2	------	I	-----	4111. 108	60	3	I	-----
4070. 297	3	------	I	-----	4111. 946	6	------	I	-----
4070. 669	3	------	I	-----	4112. 301	3	------	I	-----
4071. 006	9	------	I	-----	4113. 573	60	150	II	4
4071. 20	5	20hl	II	5	4115. 132	6	------	I	-----
4071. 438	4	------	I	-----	4115. 88	50	4	I	1
4072. 641	3	------	I	-----	4116. 385	10	------	I	-----
4072. 885	7	1	I	-----	4118. 583	100	8	I	7
4074. 34	1	------	I	-----	4118. 882	40	3	I	-----
4074. 760	2	------	I	-----	4119. 518	10	1	I	-----
4074. 92	1	------	I	-----	4120. 44	2	------	I	-----
4076. 962	4	------	I	-----	4120. 96	1	------	I	-----
4077. 80	40	2	I	-----	4123. 22	1	------	I	-----
4078. 413	90	5	I	-----	4123. 51	7	60	II	4
4078. 880	7	------	I	-----	4125. 071	5	30	II	4
4079. 380	2	------	I	-----	4127. 628	10	------	I	-----
4080. 442	200	400	II	6	4127. 788	30	200	II	4
4082. 172	5	------	I	-----	4129. 11	1	------	I	-----
4082. 477	4	------	I	-----	4129. 22	3h	------	I	-----
4082. 578	3	------	I	-----	4130. 42	1	------	I	-----
4082. 65	------	8hl	II	-----	4131. 64	1	------	I	-----
4083. 36	300	30	I	2	4132. 70	15	------	I	-----
4086. 194	1	4hl	II	-----	4134. 15	1h	------	I	-----
4087. 00	2	------	I	-----	4136. 13	1h	------	I	-----
4087. 942	50	5	I	1	4138. 304	2	------	I	-----
4088. 18	9	------	I	-----	4138. 64	8	20	II	6
4093. 160	600	1000	II	6	4138. 905	10	1	I	-----
4094. 00	10	------	I	-----	4139. 44	3	------	I	-----
4094. 66	2	------	I	-----	4140. 20	2	10	II	-----
4094. 93	9	------	I	-----	4140. 89	1	------	I	-----
4095. 49	30	2	I	-----	4141. 720	40	4	I	-----
4096. 41	1	------	I	-----	4141. 83	2	10	II	4
4097. 140	2	7	II	5	4142. 64	1	------	I	-----
4097. 43	1	------	I	-----	4142. 824	3	------	I	-----
4097. 975	30	2	I	-----	4144. 77	3	------	I	-----
4099. 17	3	------	I	-----	4145. 759	150	15	I	3
4099. 35	2	------	I	-----	4147. 84	1	------	I	-----
4099. 69	4	------	I	-----	4149. 76	1	------	I	-----
4100. 13	1	------	I	-----	4150. 93	4	------	I	-----
4100. 38	1	------	I	-----	4152. 17	1	------	I	-----
4100. 993	7	------	I	-----	4155. 347	20	2	I	-----
4101. 464	2	------	I	-----	4156. 75	6	10	II	4
4102. 22	2	------	I	-----	4157. 64	1	------	I	-----
4103. 103	8	------	I	-----	4158. 20	3	------	I	-----
4103. 578	4	------	I	-----	4158. 60	10	------	I	-----
4104. 234	150	8	I	2	4158. 910	20	100	II	4
4104. 90	1	------	I	-----	4160. 49	1	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
4160. 97	2	------	I	-----	4251. 51	6	------	I	-----
4162. 404	30	300	II	7	4256. 643	6	------	I	-----
4162. 706	100	8	I	-----	4260. 98	80	8	I	3
4163. 41	5	20	II	-----	4262. 72	8	30	II	6
4163. 90	3	------	I	-----	4263. 45	150	15	I	2
4164. 50	1h	------	I	-----	4268. 09	2	20	II	1
4165. 35	4	------	I	-----	4268. 49	4	------	I	-----
4166. 26	1h	------	I	-----	4269. 256	40	4	I	-----
4167. 24	1	------	I	-----	4269. 695	10	80	II	6
4167. 87	7	------	I	-----	4270. 42	2	------	I	-----
4168. 08	2	------	I	-----	4272. 854	40	200	II	7
4169. 02	15	------	I	-----	4275. 42	2	------	I	-----
4170. 997	20	2	I	-----	4275. 78	2	------	I	-----
4171. 248	7	------	I	-----	4276. 305	10	------	I	-----
4172. 190	8	------	I	-----	4280. 021	10	------	I	-----
4174. 348	1500	150	I	3	4280. 59	4	------	I	-----
4177. 522	20	500	II	4	4281. 89	4	------	I	-----
4177. 81	1	------	I	-----	4283. 34	3h	------	I	-----
4178. 13	1	------	I	-----	4283. 65	2	------	I	-----
4179. 51	3	100h	II	5	4287. 26	40	4	I	-----
4180. 61	3	------	I	-----	4287. 98	4	------	I	-----
4182. 59	2	------	I	-----	4292. 980	10	------	I	-----
4183. 40	1	------	I	-----	4294. 02	20	2	I	-----
4183. 69	15	1	I	-----	4294. 78	300	30	I	1
4184. 29	3	------	I	-----	4296. 45	50	5	I	7
4184. 80	3h	------	I	-----	4299. 698	7	------	I	-----
4186. 10	1	2	II	-----	4300. 03	2	------	I	-----
4186. 54	3	------	I	-----	4302. 596	4	------	I	-----
4187. 45	5	------	I	-----	4303. 661	40	3	I	-----
4187. 69	4	20	II	6	4304. 46	1	------	I	-----
4190. 95	50	5	I	3	4306. 171	15	1	I	-----
4193. 19	6	------	I	-----	4309. 362	20	2	I	-----
4195. 26	10	------	I	-----	4310. 27	1	------	I	-----
4197. 43	4	------	I	-----	4314. 35	10	------	I	-----
4201. 55	80	10	I	7	4315. 83	1	------	I	-----
4201. 75	------	5	II	-----	4317. 51	20	2	I	-----
4206. 566	50	300	II	6	4318. 138	100	10	I	2
4207. 07	20	1	I	-----	4319. 51	10	40	II	6
4207. 40	------	4	II	-----	4320. 68	40	200	II	6
4209. 743	100	10	I	7	4321. 342	10	150	II	6
4210. 59	15	------	I	-----	4321. 608	7	------	I	-----
4212. 72	10	------	I	-----	4323. 50	2	------	I	-----
4218. 01	2	------	I	-----	4323. 58	2	------	I	-----
4218. 57	2	------	I	-----	4325. 46	2	------	I	-----
4218. 83	------	3	II	----	4327. 51	5	20	II	5
4219. 40	6	------	I	-----	4328. 13	10	------	I	-----
4220. 45	4	------	I	-----	4328. 84	7	------	I	-----
4221. 765	15	------	I	-----	4330. 282	150	20	I	2
4223. 54	2	------	I	-----	4333. 75	7	------	I	-----
4226. 52	3	------	I	-----	4333. 86	30	2	I	-----
4228. 074	100	10	I	2	4334. 63	10	150	II	4
4231. 187	15	1	I	-----	4335. 15	10	20	II	5
4232. 42	10	200	II	6	4336. 656	40	500	II	6
4235. 08	3	------	I	-----	4339. 65	15	2	I	-----
4241. 90	1	40	II	5	4340. 30	30	2	I	-----
4245. 168	40	4	I	1	4342. 63	3	------	I	-----
4245. 85	4	50	II	6	4347. 113	5	------	I	-----
4246. 20	2	------	I	-----	4347. 59	2	------	I	-----
4248. 005	4	------	I	-----	4348. 332	15	------	I	-----
4249. 344	7	80	II	6	4349. 736	50	3	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity: Tube	Intensity: Spark	Spectrum	Zeeman type
A				
4350. 506	30	400	II	6
4351. 172	30	2	I	-----
4352. 567	60	7	I	1
4353. 36	30	5	I	-----
4354. 05	10	1	I	-----
4354. 16	10	------	I	-----
4356. 306	300	40	I	3
4357. 000	60	7	I	-----
4358. 70	5	------	I	-----
4359. 90	1	------	I	-----
4360. 19	7	------	I	-----
4360. 32	10	2	I	-----
4362. 12	20	2	I	-----
4362. 85	3	------	I	-----
4365. 377	60	6	I	2
4365. 679	3	40	II	6
4367. 893	70	150	II	5
4368. 83	5	------	I	-----
4370. 02	2	------	I	-----
4370. 948	80	300	II	7
4374. 44	2	------	I	-----
4376. 58	15	1	I	-----
4379. 064	40	3	I	-----
4379. 175	50	3	I	1
4380. 70	7	------	I	-----
4380. 966	7	------	I	-----
4382. 429	5	------	I	-----
4383. 88	2	------	I	-----
4384. 180	9	------	I	-----
4384. 629	7	------	I	-----
4385. 490	8	30	II	4
4386. 075	4	------	I	-----
4386. 668	3	------	I	-----
4389. 926	15	1	I	-----
4390. 720	20	2	I	-----
4391. 27	20	2	I	-----
4392. 10	1	10Hl	II	-----
4392. 311	15	1	I	-----
4396. 528	4	------	I	-----
4397. 14	3	10	II	4
4397. 382	4	------	I	-----
4397. 69	5	------	I	-----
4402. 59	------	3	II	-----
4403. 62	2	------	I	-----
4404. 14	20	3	I	-----
4406. 98	3	------	I	-----
4407. 84	2	------	I	-----
4407. 96	3	------	I	-----
4408. 81	1	3h	II	-----
4412. 386	20	3	I	-----
4415. 33	1	------	I	-----
4416. 19	40	3	I	2
4417. 37	60	300	II	7
4417. 91	150	20	I	7
4418. 247	70	9	I	3
4418. 60	10	------	I	-----
4419. 76	3	------	I	-----
4422. 26	60	6	I	-----
4422. 80	90	400	II	5
4426. 18	4	50hl	II	5
A				
4428. 459	7	------	I	-----
4429. 17	1	------	I	-----
4429. 60	4	------	I	-----
4430. 652	15	------	I	-----
4431. 155	4	------	I	-----
4431. 86	4	------	I	-----
4432. 024	7	------	I	-----
4432. 14	3	------	I	-----
4432. 78	1	------	I	-----
4434. 123	10	------	I	-----
4434. 340	20	------	I	-----
4435. 63	3	------	I	-----
4435. 95	3	------	I	-----
4437. 44	6	------	I	-----
4438. 038	200	30	I	7
4442. 40	3	------	I	-----
4443. 076	50	10	I	7
4443. 74	15	------	I	-----
4444. 07	1	------	I	-----
4445. 92	4	------	I	-----
4448. 086	15	------	I	-----
4448. 41	1	------	I	-----
4448. 76	2	10Hl	I	-----
4452. 67	6	40	II	7
4452. 92	80	8	I	3
4453. 728	10	------	I	-----
4454. 582	7	------	I	-----
4457. 347	300	40	I	2
4459. 992	15	1	I	-----
4461. 181	200	30	I	1
4462. 465	10	------	I	-----
4464. 29	5	------	I	-----
4465. 196	2	------	I	-----
4466. 39	15	150	II	5
4466. 88	1	------	I	-----
4468. 882	10	------	I	-----
4468. 96	2	------	I	-----
4473. 042	20	3	I	-----
4473. 313	15	1	I	-----
4473. 72	1	------	I	-----
4474. 063	5	------	I	-----
4474. 511	15	2	I	-----
4477. 60	5	------	I	-----
4478. 824	3	------	I	-----
4478. 94	2	------	I	-----
4480. 044	4	------	I	-----
4481. 38	1	------	I	-----
4482. 20	10	------	I	-----
4482. 57	2	------	I	-----
4482. 86	1	------	I	-----
4483. 28	3	20	II	7
4483. 61	2	------	I	-----
4485. 253	15	2	I	-----
4486. 126	40	150	II	6
4486. 612	3	80hl	II	6
4487. 057	2	------	I	-----
4488. 00	1	------	I	-----
4489. 03	1	------	I	-----
4490. 580	10	70	II	5
4490. 90	1	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
4491. 37	1	------	I	-----
4492. 16	30	2	I	2
4493. 23	2	------	I	-----
4494. 235	3	------	I	-----
4495. 08	1	------	I	-----
4495. 83	2	------	I	-----
4496. 474	10	------	I	-----
4497. 52	1	------	I	-----
4498. 94	8	------	I	-----
4499. 662	50	5	I	3
4501. 49	3	------	I	-----
4501. 78	2h	------	I	-----
4502. 01	4	------	I	-----
4503. 095	15	------	I	-----
4504. 01	1	------	I	-----
4504. 328	4	------	I	-----
4506. 669	15	2	I	-----
4508. 874	2	5	II	-----
4510. 52	1	------	I	-----
4510. 96	2	------	I	-----
4511. 970	3	------	I	-----
4512. 51	1	------	I	-----
4512. 60	1	------	I	-----
4512. 87	1	------	I	-----
4513. 62	2h	------	I	-----
4514. 35	2	------	I	-----
4514. 603	5	------	I	-----
4517. 068	10	------	I	-----
4517. 32	3	------	I	-----
4518. 305	50	5	I	3
4518. 98	3	60h	II	6?
4519. 69	2	------	I	-----
4520. 587	30	4	I	7
4521. 477	4	------	I	-----
4522. 182	8	1	I	-----
4523. 32	4	------	I	-----
4523. 575	4	------	I	-----
4524. 728	10	200	II	-----
4525. 92	15	------	I	6
4527. 31	1	------	I	-----
4527. 67	1	------	I	-----
4527. 95	2	------	I	-----
4530. 133	12	------	I	-----
4531. 14	1	------	I	-----
4531. 87	1d	------	I	-----
4532. 74	2	------	I	-----
4533. 165	30	100	II	5
4534. 77	1	------	I	-----
4535. 37	10	100	II	-----
4537. 548	10	------	I	5
4539. 76	3	7	II	-----
4540. 934	200	20	I	-----
4541. 29	10	60	II	7
4541. 71	40	4	I	6
4543. 01	20	3	I	-----
4544. 02	100	10	I	-----
4544. 775	1	------	I	7
4546. 90	10	1	I	-----
4546. 98	15	2	I	-----
4547. 87	30	2	I	7
				3
A				
4550. 16	40	3	I	7
4550. 576	8	1	I	-----
4553. 776	80	8	I	7
4556. 85	9	------	I	-----
4559. 76	20	2	I	3
4561. 12	2	------	I	-----
4561. 57	2	------	I	-----
4561. 84	1	------	I	-----
4562. 638	15	1	I	-----
4563. 75	1	30hl	II	7
4565. 95	300	50	I	7
4569. 910	7	------	I	1
4570. 510	8	------	I	-----
4570. 680	10	150hl	II	-----
4573. 80	20	100	II	4
4575. 05	1	------	I	4
4576. 60	1	------	I	-----
4577. 06	1	------	I	-----
4577. 78	2	------	I	-----
4578. 18	2	------	I	-----
4579. 05	2	------	I	-----
4579. 38	8	------	I	-----
4581. 030	10	------	I	-----
4582. 08	1	------	I	-----
4582. 26	1	------	I	-----
4583. 53	1	------	I	-----
4583. 86	2	------	I	-----
4585. 00	1	------	I	-----
4585. 10	2	------	I	-----
4586. 240	20	70	II	6
4588. 22	5	------	I	-----
4588. 81	1	------	I	-----
4589. 13	3	------	I	-----
4590. 537	40	4	I	-----
4592. 70	1	------	I	-----
4597. 945	60	6	I	7
4598. 801	300	30	I	2
4598. 92	200	20	I	-----
4599. 44	15	150	II	6
4602. 61	2	40hl	II	4
4602. 75	30	4	I	-----
4603. 524	15	------	I	-----
4604. 97	3hl	------	I	-----
4605. 309	4	------	I	-----
4605. 782	20	80	II	5
4606. 07	4hl	------	I	-----
4606. 75	6	------	I	-----
4606. 91	5	20Hl	II	-----
4607. 48	5h	------	I	-----
4608. 093	100	10	I	1
4610. 288	2	------	I	-----
4611. 63	1d	------	I	-----
4612. 29	9	------	I	-----
4613. 222	3	------	I	-----
4613. 744	15	300	II	6
4614. 192	40	4	I	-----
4614. 60	10	1	I	-----
4617. 78	2	------	I	-----
4619. 52	20	2	I	7
4620. 862	300	30	I	2

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
4622.705	20	300	II		4692.706	4	------	I	
4626.36	7	20	II	5	4693.422	5	------	I	
4627.07	3h	------	I		4693.56	5	------	I	
4629.002	7	------	I		4695.49	1	------	I	
4630.608	40	------	I	3	4698.439	8	------	I	
4632.042	10	------	I		4699.008	150	30	I	7
4633.25	1	------	I		4699.716	15	300	II	5
4635.60	2	------	I		4700.30	1	------	I	
4636.52	15	------	I		4702.89	2	------	I	
4637.06	1	------	I		4703.116	1	4	II	
4637.16	1	------	I		4703.60	12	100	II	5
4637.39	1	------	I		4704.21	4	------	I	
4640.12	10	200	II	5	4706.06	12	------	I	
4642.25	30	4	I	1	4707.59	2	------	I	
4643.14	3h	------	I		4708.053	30	4	I	7
4643.61	1	------	I		4708.85	40	5	I	3
4644.57	1	------	I		4709.762	15	2	I	
4645.23	1	------	I		4711.022	12	------	I	
4645.40	3	------	I		4712.205	20	2	I	
4647.47	2	------	I		4712.296	10	------	I	
4648.35	10	------	I	3	4713.47	2	10	II	
4650.59	20	2	I	7	4713.68	3	------	I	
4650.94	5	------	I		4713.82	1	------	I	
4651.13	1	------	I		4714.67	1	------	I	
4651.766	5	------	I		4714.99	6	20	II	6
4652.258	20	2	I		4716.42	2	------	I	
4655.198	300	50	I	**3**	4717.43	30	2	I	
4655.53	5	30h	II		4719.11	30	200	II	6
4659.219	4	40	II	6	4720.25	2	------	I	
4660.86	6	------	I		4720.86	7	------	I	
4661.75	3	------	I		4721.32	2	------	I	
4663.187	8	------	I		4721.71	50	5	I	2
4664.134	60	400	II	4	4722.46	2	------	I	
4667.292	30	2	I		4722.95	3	------	I	
4668.23	1	------	I		4724.21	2	------	I	
4669.245	50	7	I	3	4724.54	1	------	I	
4670.94	20	2	I	3	4725.60	2	------	I	
4671.82	2	------	I		4727.567	5	------	I	
4672.43	3	10	II		4728.42	6	------	I	
4673.176	20	2	I	0	4729.37	1	------	I	
4673.318	8	------	I		4729.81	3	------	I	
4675.454	7	150hl	II	5	4730.396	7	------	I	
4676.71	3	------	I		4730.648	15	------	I	
4677.35	2	------	I		4731.36	20	200	II	4
4677.61	2	------	I		4731.72	1	------	I	
4678.43	1	------	I		4733.72	3	15	II	5
4681.22	1	------	I		4734.29	3	------	I	
4681.86	8	------	I		4735.51	40	4	I	
4682.29	1	------	I		4735.66	10	30	II	6
4682.66	4	70	II	4	4735.88	3	15	II	
4683.94	40	6	I		4737.67	4	------	I	
4684.33	4	------	I		4738.112	20	3	I	
4685.36	2	------	I		4738.23	4	------	I	
4686.388	30	4	I		4738.574	80	10	I	2
4687.155	8	------	I		4739.83	40	4	I	
4687.42	4	------	I		4741.02	10	------	I	
4688.37	40	8	I		4741.13	4	------	I	
4688.99	4	------	I		4742.530	10	------	I	
4690.48	1	------	I		4742.92	1	------	I	
4691.453	9	------	I		4743.20	1	------	I	

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
4746. 78	6	------	I	-----	4808. 70	10	------	I	-----
4748. 35	10	------	I	-----	4809. 189	5	30	II	-----
4748. 409	15	1	I	-----	4810. 11	3	------	I	-----
4748. 89	1	------	I	-----	4811. 146	40	5	I	1
4749. 39	1	6	II	-----	4812. 19	1h	------	I	-----
4750. 66	7	------	I	-----	4813. 500	7	------	I	-----
4751. 492	15	------	I	-----	4814. 62	1	------	I	-----
4753. 124	10	------	I	-----	4814. 79	2	------	I	-----
4753. 89	3	------	I	-----	4814. 91	2	------	I	-----
4753. 97	4	------	I	-----	4817. 227	20	400	II	4
4756. 08	3d	------	I	-----	4818. 84	100	15	I	2
4756. 35	2	------	I	-----	4822. 43	1	------	I	-----
4756. 94	1h	------	I	-----	4823. 80	3	------	I	-----
4757. 611	50	5	I	7	4823. 98	1	------	I	-----
4758. 789	6	------	I	-----	4824. 38	3	------	I	-----
4760. 55	5	100hl	II	6	4824. 50	2	------	I	-----
4760. 907	7	------	I	-----	4825. 37	2h	------	I	-----
4765. 75	5	80	II	-----	4825. 85	1	6hl	II	-----
4766. 507	100	10	I	7	4826. 50	1	------	I	-----
4768. 23	2h	------	I	-----	4826. 89	1	10hl	II	-----
4769. 372	20	2	I	3	4827. 57	1h	------	I	-----
4769. 83	1	------	I	-----	4828. 58	1h	------	I	-----
4770. 58	1	------	I	-----	4828. 97	5	------	I	-----
4771. 262	4	------	I	-----	4830. 45	3H	------	I	-----
4773. 262	15	2	I	-----	4832. 25	------	5hl	II	-----
4773. 72	150	20	I	7	4834. 20	80	10	I	3
4774. 904	30	4	I	7	4834. 78	------	20hl	II	-----
4774. 994	7	------	I	-----	4835. 32	7	------	I	-----
4776. 50	1	------	I	-----	4837. 238	150	20	I	2
4777. 216	20	2	I	1	4837. 80	12	1	I	-----
4779. 66	6	------	I	-----	4838. 740	8	------	I	-----
4782. 737	200	50	I	1	4838. 79	6	------	I	-----
4783. 392	3	------	I	-----	4839. 12	2	------	I	-----
4783. 83	3	------	I	-----	4839. 29	1	------	I	-----
4784. 80	5	------	I	-----	4839. 82	7	------	I	-----
4785. 17	2	------	I	-----	4841. 51	3H	------	I	-----
4786. 16	1	------	I	-----	4842. 185	15	1	I	-----
4787. 42	3	------	I	-----	4842. 984	3	------	I	-----
4787. 52	1	------	I	-----	4844. 00	15	50	II	5
4787. 62	1	------	I	-----	4844. 19	10	------	I	-----
4788. 966	7	------	I	-----	4846. 02	1	------	I	-----
4790. 73	10	300	II	5	4846. 91	1	------	I	-----
4791. 26	7	------	I	-----	4848. 458	5	150	II	4
4791. 588	9	------	I	-----	4849. 19	1	------	I	-----
4792. 45	1	------	I	-----	4850. 60	40	4	I	7?
4793. 11	5h	------	I	-----	4851. 69	1	------	I	-----
4793. 52	3	------	I	-----	4852. 53	5	------	I	-----
4794. 00	4h	------	I	-----	4853. 58	1	------	I	-----
4794. 89	3h	------	I	-----	4853. 993	3	------	I	-----
4795. 98	15	2	I	3	4857. 01	1	5h	II	-----
4796. 88	2	------	I	-----	4857. 17	1	------	I	-----
4797. 69	3	------	I	-----	4858. 42	70	7	I	1
4798. 49	1	------	I	-----	4859. 24	200	30	I	7
4800. 50	500	100	I	2	4860. 52	3	8hl	II	-----
4804. 05	2	------	I	-----	4860. 91	2	------	I	-----
4805. 076	10	------	I	-----	4861. 51	10	------	I	-----
4805. 27	4	------	I	-----	4863. 282	150	20	I	2
4805. 55	1	------	I	-----	4864. 17	2	------	I	-----
4805. 723	3	------	I	-----	4865. 08	2	------	I	-----
4807. 14	15	80	II	6	4865. 43	4	100	II	4

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
4865. 546	2	------	I	-----	4925. 214	15	1	I	-----
4865. 82	1	------	I	-----	4926. 189	30	2	I	-----
4866. 33	3	------	I	-----	4926. 594	10	2	I	-----
4868. 84	1	------	I	-----	4926. 983	8	30	II	4
4872. 949	50	5	I	1	4927. 15	2	------	I	-----
4875. 63	1	------	I	-----	4927. 60	2h	------	I	-----
4875. 76	1	------	I	-----	4928. 194	6	------	I	-----
4875. 92	2	------	I	-----	4929. 55	1	------	I	-----
4877. 587	150	20	I	7	4932. 260	7	------	I	2
4878. 166	20	4	I	7	4934. 458	30	150	II	4
4881. 27	1	------	I	-----	4934. 595	6	------	I	-----
4881. 74	3	------	I	-----	4936. 35	3	------	I	-----
4882. 48	2	------	I	-----	4937. 810	5	------	I	-----
4882. 649	2	8hl	II	-----	4938. 717	3	------	I	-----
4883. 21	1	15hl	II	-----	4942. 74	1	------	I	-----
4883. 66	2	------	I	-----	4943. 42	15	2	I	7
4884. 258	10	------	I	-----	4944. 82	10	1	I	-----
4884. 65	10	------	I	-----	4945. 370	7	40	II	5
4885. 69	2	40hl	II	4	4945. 84	3	------	I	-----
4886. 47	4	------	I	-----	4947. 336	15	2	I	3
4886. 84	1	------	I	-----	4948. 951	100	15	I	3
4887. 73	1	------	I	-----	4950. 02	3h	------	I	-----
4888. 05	3	------	I	-----	4950. 36	1	------	I	-----
4889. 609	7	1	I	-----	4950. 69	2	------	I	-----
4889. 932	20	2	I	2	4951. 095	4	------	I	-----
4890. 754	6	------	I	-----	4955. 65	1	------	I	-----
4892. 993	5	------	I	-----	4955. 94	1	------	I	-----
4893. 62	2	------	I	-----	4956. 813	5	------	I	-----
4894. 82	1	------	I	-----	4958. 24	2	------	I	-----
4895. 086	5	------	I	-----	4960. 074	5	------	I	-----
4895. 301	6	------	I	-----	4960. 32	1	------	I	-----
4895. 48	1	------	I	-----	4960. 53	------	4h	II	-----
4896. 34	40	4	I	3	4962. 381	50	6	I	1
4897. 26	2	------	I	-----	4964. 740	4	------	I	-----
4898. 38	1	------	I	-----	4965. 28	2	------	I	-----
4898. 73	3	------	I	-----	4965. 83	2	------	I	-----
4900. 179	8	1	I	-----	4966. 03	1	------	I	-----
4901. 356	6	------	I	-----	4967. 616	5	------	I	-----
4901. 44	4	------	I	-----	4975. 26	400	50	I	7
4901. 767	5	------	I	-----	4978. 724	4	------	I	-----
4903. 06	20	2	I	2	4981. 73	2	------	I	-----
4904. 480	7	300h	II	4	4982. 72	2h	------	I	-----
4906. 17	8	1	I	-----	4983. 07	1h	------	I	-----
4906. 400	6	2	I	7	4983. 70	3h	------	I	-----
4907. 079	6	------	I	-----	4984. 766	3	15	II	6
4907. 244	6	------	I	-----	4985. 17	2	------	I	-----
4907. 33	3	15h	II	6	4985. 33	3	------	I	-----
4907. 56	3	------	I	-----	4986. 37	1	------	I	-----
4908. 30	1	------	I	-----	4986. 55	1	------	I	-----
4910. 10	30	2	I	2	4987. 28	1	------	I	-----
4911. 40	1	------	I	-----	4988. 712	2	------	I	-----
4912. 11	5	------	I	-----	4988. 88	1	------	I	-----
4914. 888	7	------	I	-----	4991. 06	1	------	I	-----
4915. 32	40	6	I	3	4994. 795	4h	------	I	-----
4916. 98	8	------	I	-----	4995. 831	2	------	I	-----
4918. 094	4	------	I	-----	4998. 03	4hs	------	I	-----
4920. 16	2	------	I	-----	4998. 76	1	------	I	-----
4920. 95	10	40Hl	II	7	4999. 21	7	------	I	-----
4923. 92	2	------	I	-----	4999. 702	30	100	II	5
4924. 54	1	------	I	-----	5000. 54	20	2	I	3

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
5000. 81	1	------	I	-----	5082. 21	3	------	I	-----
5001. 96	3	------	I	-----	5082. 770	2	------	I	-----
5002. 06	2h	------	I	-----	5084. 74	1	------	I	-----
5004. 50	1	------	I	-----	5085. 07	2	------	I	-----
5005. 18	2	------	I	-----	5086. 482	4	------	I	-----
5007. 21	1	------	I	-----	5086. 96	10	1	I	-----
5007. 94	2	------	I	-----	5087. 37	2	------	I	-----
5008. 068	3	------	I	-----	5087. 46	2	------	I	-----
5011. 01	1h	------	I	-----	5089. 50	1	------	I	-----
5012. 185	10	1	I	-----	5090. 876	15	2	I	3
5012. 89	1h	------	I	-----	5090. 996	6	------	I	-----
5013. 82	1	8Hl	II	-----	5091. 28	3	------	I	-----
5014. 28	1	------	I	-----	5093. 698	5	------	I	-----
5018. 20	200	20	I	1	5094. 117	2	------	I	-----
5021. 13	40	5	I	2	5094. 683	5	------	I	-----
5021. 745	40	5	I	2	5096. 21	1	------	I	-----
5023. 09	70	5	I	2	5097. 40	1	------	I	-----
5025. 91	15	1	I	3	5097. 74	2	------	I	-----
5029. 46	3	------	I	-----	5098. 80	2	------	I	-----
5029. 71	2	------	I	-----	5100. 64	60	4	I	1
5929. 99	1h	------	I	-----	5101. 668	40	4	I	1
5033. 32	1	------	I	-----	5102. 634	2	------	I	-----
5034. 14	2	------	I	-----	5105. 64	1	------	I	-----
5034. 33	4	30	II	5	5107. 319	4	------	I	-----
5034. 92	30	3	I	7	5108. 55	1	------	I	-----
5035. 50	1	------	I	-----	5109. 04	1h	------	I	-----
5035. 899	6	------	I	-----	5110. 56	2	50hl	II	4
5037. 74	9	------	I	7	5111. 148	20	2	I	-----
5038. 08	3	------	I	-----	5112. 130	100	10	I	1
5039. 15	3	------	I	-----	5117. 09	10	------	I	-----
5040. 202	15	------	I	-----	5122. 727	4	------	I	-----
5040. 815	50	400	II	4	5126. 81	3	------	I	-----
5042. 30	1	------	I	-----	5127. 05	------	5h	II	-----
5043. 102	2	------	I	-----	5128. 116	8	------	I	-----
5047. 440	300	30	I	2	5128. 504	20	100	II	4
5049. 915	1	20h	II	4	5128. 96	------	6hl	II	-----
5051. 319	50	3	I	3	5130. 28	1	------	I	-----
5053. 68	2	------	I	-----	5131. 38	1	------	I	-----
5055. 93	2	------	I	-----	5133. 10	15	------	I	-----
5056. 89	10	------	I	-----	5133. 66	1	------	I	-----
5057. 037	5	80h	II	6	5135. 81	5	------	I	-----
5058. 166	7	40	II	6	5136. 20	30	2	I	1
5058. 778	4	------	I	-----	5136. 52	2	------	I	-----
5060. 584	5	------	I	-----	5137. 86	1	------	I	-----
5061. 80	3h	------	I	-----	5139. 51	5h	------	I	-----
5064. 15	3h	------	I	-----	5140. 202	4	------	I	-----
5064. 67	2	------	I	-----	5141. 044	5	------	I	-----
5067. 65	2h	------	I	-----	5141. 19	2	------	I	-----
5068. 62	------	7Hl	II	-----	5141. 81	2h	------	I	-----
5069. 810	20	1	I	1	5142. 997	9	------	I	-----
5071. 21	5	40	II	4	5144. 30	2	------	I	-----
5072. 295	8	1	I	-----	5145. 22	2h	------	I	-----
5073. 131	4	------	I	-----	5145. 72	2	------	I	-----
5074. 72	1	7Hl	II	-----	5146. 14	1	7hl	II	-----
5075. 920	10	50	II	6	5147. 401	7	------	I	-----
5076. 29	2	------	I	-----	5148. 62	1h	------	I	-----
5077. 614	6	------	I	-----	5148. 899	8	------	I	-----
5079. 629	20	300	II	5	5153. 122	40	4	I	4
5080. 406	2	40	II	4	5156. 04	1	50hl	II	6
5081. 77	10	1	I	-----	5157. 21	5	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
5157. 95	200	20	I	1	5241. 697	4	------	I	-----
5160. 05	2	------	I	-----	5243. 460	40	3	I	-----
5161. 570	15	2	I	-----	5243. 984	250	30	I	1
5162. 32	1	------	I	-----	5244. 67	50	4	I	7
5164. 15	2	------	I	-----	5247. 031	40	3	I	-----
5164. 516	2	50hl	II	6	5247. 130	15	400	II	7
5166. 390	20	2	I	3	5249. 12	1	------	I	-----
5167. 376	30	4	I	2	5250. 11	2	------	I	-----
5168. 23	2	------	I	-----	5251. 309	7	------	I	-----
5170. 173	100	20	I	1	5252. 452	9	1	I	-----
5171. 02	10h	------	I	-----	5252. 91	2	------	I	-----
5171. 44	3h	------	I	-----	5253. 615	10	1	I	-----
5171. 76	2h	------	I	-----	5254. 48	20	3	I	2
5172. 15	2	------	I	-----	5255. 09	2	------	I	-----
5172. 67	2	------	I	-----	5255. 464	15	------	I	7
5173. 162	15	2	I	7	5255. 71	------	8hl	II	-----
5176. 614	1	------	I	-----	5258. 736	40	5	I	3
5177. 644	10	1	I	-----	5260. 43	30	150	II	7
5177. 860	4	------	I	-----	5262. 60	4	------	I	-----
5178. 02	2	------	I	-----	5264. 942	40	300	II	6
5181. 87	300	60	I	2	5266. 72	1	------	I	-----
5182. 90	8	------	I	-----	5268. 37	1	------	I	-----
5184. 295	20	2	I	3	5268. 88	2	------	I	-----
5186. 13	3h	------	I	-----	5271. 38	2	------	I	-----
5186. 825	50	10	I	7	5272. 53	8	------	I	-----
5187. 732	20	150	II	4	5274. 018	8	1	I	-----
5189. 38	4h	------	I	-----	5275. 04	150	20	I	7
5190. 28	1	------	I	-----	5275. 81	3h	------	I	-----
5191. 168	4	------	I	-----	5276. 22	1	------	I	-----
5191. 46	2	------	I	-----	5276. 355	1	20Hl	II	7
5192. 234	7	------	I	-----	5277. 16	10	1	I	-----
5192. 58	1	------	I	-----	5280. 03	1	------	I	-----
5192. 99	1	------	I	-----	5281. 07	3	------	I	-----
5193. 63	3	------	I	-----	5284. 06	1	------	I	-----
5194. 567	7	20h	II	6	5284. 28	1	------	I	-----
5196. 46	1	------	I	-----	5284. 591	10	1	I	-----
5199. 545	10	1	I	1	5286. 098	70	7	I	3
5200. 866	20	2	I	1?	5288. 40	1	------	I	-----
5208. 84	15	2	I	-----	5289. 97	3	100hl	II	1
5212. 045	3	------	I	-----	5290. 212	10	1	I	-----
5212. 325	7	1	I	-----	5290. 812	20	2	I	1
5214. 549	1	8h	II	-----	5292. 783	30	3	I	1
5216. 40	3	------	I	-----	5294. 870	300	30	I	7
5217. 26	2	------	I	-----	5298. 063	70	500	II	7
5220. 201	1	------	I	-----	5299. 84	10	60	II	6
5222. 43	10	1	I	7	5300. 09	4	------	I	-----
5225. 23	6	------	I	-----	5300. 18	1	------	I	-----
5225. 755	4	------	I	-----	5303. 35	2	------	I	-----
5226. 03	1h	------	I	-----	5304. 178	40	4	I	3
5226. 64	1h	------	I	-----	5304. 44	1	------	I	-----
5226. 89	1h	------	I	-----	5305. 83	4	------	I	-----
5227. 30	2h	------	I	-----	5307. 812	60	8	I	2
5229. 594	6	------	I	-----	5309. 681	100	15	I	2
5230. 04	1h	------	I	-----	5311. 598	80	500	II	7
5232. 315	3	------	I	-----	5314. 016	2	------	I	-----
5239. 15	1	------	I	-----	5315. 578	7	------	I	-----
5240. 05	1	------	I	-----	5315. 928	15	1	I	3
5240. 424	10	1	I	-----	5316. 888	6	------	I	-----
5240. 90	1	------	I	-----	5317. 82	2	------	I	-----
5241. 040	3	------	I	-----	5320. 22	2	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
5322. 365	9	------	I	-----	5405. 23	2	------	I	-----
5324. 035	7	------	I	-----	5410. 27	2	------	I	-----
5324. 25	15	100hl	II	5	5411. 806	2	------	I	-----
5324. 59	2	------	I	-----	5412. 17	4	------	I	-----
5324. 78	1	------	I	-----	5415. 99	1	------	I	-----
5327. 31	1	------	I	-----	5418. 75	1	------	I	-----
5327. 89	3	------	I	-----	5419. 305	3	------	I	-----
5328. 89	10	------	I	-----	5420. 408	2	15hl	II	6
5330. 85	1	------	I	-----	5420. 84	1	------	I	-----
5331. 94	2	------	I	-----	5421. 21	2	------	I	-----
5332. 40	1	------	I	-----	5421. 91	1	------	I	-----
5334. 34	6	1	I	-----	5423. 37	1	------	I	-----
5337. 10	2	------	I	-----	5423. 981	60	9	I	2
5338. 386	8	1	I	-----	5426. 35	1h	------	I	-----
5340. 027	2	------	I	-----	5428. 304	15	2	I	-----
5341. 48	1	------	I	-----	5430. 034	2	15hl	II	5
5341. 956	2	------	I	-----	5430. 17	1	------	I	-----
5343. 75	1	------	I	-----	5430. 708	7	------	I	-----
5343. 99	1	------	I	-----	5432. 732	2	------	I	-----
5344. 31	1	------	I	-----	5433. 190	6	------	I	-----
5344. 93	1	------	I	-----	5433. 728	7	------	I	-----
5345. 40	1	------	I	-----	5434. 20	1	------	I	-----
5346. 283	10	400	II	6	5434. 74	6	------	I	-----
5347. 00	1	------	I	-----	5434. 970	6	------	I	-----
5347. 65	1	------	I	-----	5435. 781	30	4	I	7
5348. 394	15	70	II	6	5438. 75	100	10	I	2
5349. 774	4	------	I	-----	5439. 698	15	2	I	-----
5354. 724	200	40	I	1	5441. 93	2h	------	I	-----
5357. 355	10	------	I	-----	5442. 565	5	------	I	-----
5358. 338	40	6	I	2	5442. 950	3	------	I	-----
5358. 54	4	------	I	-----	5444. 055	15	200	II	7
5360. 33	2	------	I	-----	5445. 06	1	------	I	-----
5361. 02	1	------	I	-----	5445. 23	1	------	I	-----
5361. 35	1	15hl	II	6	5448. 55	1	------	I	-----
5361. 466	3	------	I	-----	5448. 86	1	2h	II	-----
5366. 764	2	------	I	-----	5450. 42	1	------	I	-----
5368. 52	20	2	I	7	5450. 56	1	------	I	-----
5370. 804	9	1	I	-----	5450. 978	3	------	I	-----
5371. 112	15	2	I	-----	5451. 50	1	------	I	-----
5371. 767	2	30hl	II	4	5452. 02	2h	------	I	-----
5373. 863	300	50	I	2	5452. 92	300	30	I	7
5376. 302	10	1	I	7	5456. 542	7	------	I	-----
5381. 02	2	------	I	-----	5463. 31	150	20	I	7
5382. 083	2	------	I	-----	5463. 36	10	100	II	5
5383. 04	40	4	I	1	5465. 73	20	2	I	3
5384. 65	3h	------	I	-----	5467. 32	10	1	I	1
5385. 26	2	------	I	-----	5468. 66	1	------	I	-----
5385. 37	2	------	I	-----	5470. 149	6	------	I	-----
5389. 336	100	20	I	7	5470. 66	1	------	I	-----
5391. 343	10	60	II	6	5471. 290	3	------	I	-----
5391. 59	3	------	I	-----	5474. 54	1	4h?	II	-----
5393. 122	8	------	I	-----	5480. 633	2	------	I	-----
5394. 896	20	3	I	2	5480. 83	1	------	I	-----
5396. 11	4	------	I	-----	5485. 778	8	------	I	-----
5397. 484	3	------	I	-----	5486. 12	2	------	I	-----
5398. 655	10	1	I	3	5486. 72	1	------	I	-----
5399. 40	1	------	I	-----	5488. 40	3	------	I	-----
5403. 60	2h	------	I	-----	5488. 87	2	------	I	-----
5404. 457	50	7	I	3	5490. 48	1	------	I	-----
5405. 12	1	------	I	-----	5491. 87	1	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity: Tube	Intensity: Spark	Spectrum	Zeeman type	Wavelength in air	Intensity: Tube	Intensity: Spark	Spectrum	Zeeman type
A					*A*				
5492. 287	3	------	I	-----	5568. 76	1	------	I	-----
5492. 56	1	------	I	-----	5569. 61	3	------	I	-----
5492. 89	1	------	I	-----	5572. 30	4	------	I	-----
5493. 212	3	60hl	II	4	5573. 529	6	------	I	-----
5494. 54	2	------	I	-----	5575. 158	8	------	I	-----
5497. 301	50	5	I	2	5575. 857	200	30	I	3
5498. 70	1	------	I	-----	5578. 008	15	2	I	3
5501. 01	1	------	I	-----	5578. 35	1	------	I	-----
5501. 53	4	------	I	-----	5579. 90	1	------	I	-----
5502. 63	10	1	I	-----	5580. 148	8	------	I	-----
5503. 294	20	2	I	-----	5580. 69	1	------	I	-----
5506. 20	1	------	I	-----	5581. 45	9	1	I	-----
5510. 116	60	6	I	1	5583. 934	10	1	I	-----
5510. 436	40	7	I	7	5585. 013	2	------	I	-----
5512. 302	10	1	I	-----	5589. 54	1	------	I	-----
5513. 28	1	------	I	-----	5590. 691	3	9hl	II	6
5513. 97	1	------	I	-----	5594. 98	1	------	I	-----
5514. 998	3	10	II	5	5595. 60	5	------	I	-----
5516. 75	1	------	I	-----	5595. 73	3	------	I	-----
5517. 09	2	------	I	-----	5597. 546	8	------	I	-----
5517. 73	1	------	I	-----	5599. 08	5	------	I	-----
5518. 443	10	1	I	-----	5599. 42	1	------	I	-----
5520. 01	10	1	I	1	5600. 192	6	------	I	-----
5521 75	5	------	I	-----	5600. 762	60	6	I	2
5522. 05	------	2h	II	-----	5601. 15	3	------	I	-----
5522. 554	20	2	I	7	5602. 03	1	------	I	-----
5522. 84	1	------	I	-----	5606. 07	1	------	I	-----
5523. 55	3	------	I	-----	5606. 613	20	2	I	3
5524. 348	40	200	II	5	5609. 05	2	------	I	-----
5524. 95	10	1	I	-----	5609. 38	2	------	I	-----
5525. 01	10	------	I	-----	5611. 61	6	------	I	-----
5525. 631	7	1	I	-----	5613. 259	400	70	I	7
5529. 01	20	------	I	-----	5614. 004	80	10	I	?
5530. 268	30	2	I	7	5615. 63	2	------	I	-----
5531. 19	1	------	I	-----	5615. 84	1	------	I	-----
5531. 334	5	------	I	-----	5618. 57	2	------	I	-----
5532. 23	5	------	I	-----	5624. 45	1	------	I	-----
5534. 638	8	1	I	3	5625. 66	1	------	I	-----
5535. 31	1	------	I	-----	5628. 293	40	4	I	1
5535. 47	2	------	I	-----	5630. 10	1	------	I	-----
5538. 023	200	20	I	-----	5631. 13	1	------	I	-----
5538. 275	150	15	I	-----	5631. 319	2	20hl	II	7
5538. 559	20	2	I	-----	5631. 55	3	------	I	-----
5539. 51	1	------	I	-----	5631. 93	1	4	II	-----
5541. 03	1	------	I	-----	5632. 84	3	------	I	-----
5541. 920	15	2	I	3	5633. 02	2	------	I	-----
5545. 26	1	------	I	-----	5633. 450	20	2	I	1
5545. 609	4	------	I	-----	5633. 95	10	------	I	-----
5547. 83	------	8hl	II	-----	5634. 45	3h	------	I	-----
5548. 127	9	1	I	-----	5635. 81	2h	------	I	-----
5550. 61	1000	100	I	3	5635. 92	2h	------	I	-----
5552. 128	1000	100	I	1	5636. 570	2	8h	II	-----
5561. 69	3	------	I	-----	5637. 555	2	------	I	-----
5561. 77	2	------	I	-----	5638. 51	1	------	I	-----
5563. 19	3	------	I	-----	5641. 39	1	------	I	-----
5563. 32	2	------	I	-----	5642. 65	1	------	I	-----
5565. 54	2	20hl	II	6	5644. 67	30	3	I	1
5566. 87	2	------	I	-----	5645. 61	3	------	I	-----
5567. 22	1	------	I	-----	5648. 563	5	------	I	-----
5568. 44	2	------	I	-----	5649. 229	2	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
5650. 811	50	6	I	3	5745. 22	2	------	I	-----
5654. 645	80	9	I	3	5748. 72	80	9	I	3
5658. 777	1	10hl	II	-----	5751. 510	3	------	I	-----
5660. 38	1	7hl	II	-----	5751. 718	4	------	I	-----
5660. 97	1	------	I	-----	5752. 18	3	------	I	-----
5662. 078	40	4	I	1	5752. 531	2	20hl	II	6
5662. 982	20	2	I	2	5756. 51	3	------	I	-----
5664. 37	------	6hl	II	-----	5756. 83	10	------	I	-----
5664. 824	4	------	I	-----	5758. 96	10	------	I	-----
5668. 716	20	2	I	2	5762. 41	2	------	I	-----
5673. 565	4	100hl	II	7	5765. 37	40	4	I	2
5677. 210	8	------	I	-----	5765. 96	30	4	I	7
5679. 553	30	------	I	2	5766. 50	------	2	II	-----
5680. 444	10	------	I	-----	5767. 20	20	60	II	6
5681. 110	4	------	I	-----	5771. 397	15	------	I	-----
5682. 34	2	------	I	-----	5773. 33	1	------	I	-----
5682. 47	1	------	I	-----	5774. 016	8	------	I	-----
5683. 738	6	------	I	7	5774. 89	3	------	I	-----
5684. 807	15	1	I	-----	5776. 00	1	------	I	-----
5686. 18	1	------	I	-----	5778. 92	1	------	I	-----
5688. 12	15	------	I	-----	5780. 46	------	7	II	-----
5688. 81	1	2	II	-----	5784. 75	2h	------	I	-----
5689. 77	1	8hl	II	-----	5791. 71	10	------	I	-----
5690. 41	1	------	I	-----	5794. 72	10	------	I	-----
5690. 58	1	------	I	-----	5796. 329	30	2	I	3?
5691. 15	1	------	I	-----	5799. 760	50	5	I	3
5691. 914	3	------	I	-----	5800. 567	4	------	I	-----
5692. 72	1	------	I	-----	5801. 693	5	70	II	7
5693. 02	4	------	I	-----	5801. 83	6	------	I	-----
5694. 34	5	------	I	-----	5802. 88	40	3	I	3
5695. 732	8	1	I	-----	5803. 64	2	------	I	-----
5697. 25	15	2	I	3	5804. 84	1	------	I	-----
5699. 46	4	------	I	-----	5806. 28	1	------	I	-----
5700. 82	1	------	I	-----	5808. 428	30	2	I	-----
5701. 11	4	------	I	-----	5809. 27	5	------	I	-----
5702. 10	20	2	I	1	5809. 499	40	100	II	6
5703. 95	2h	------	I	-----	5810. 26	2	------	I	-----
5706. 64	5	------	I	-----	5810. 58	2	------	I	-----
5706. 85	2	------	I	-----	5811. 275	15	2	I	-----
5708. 38	10	------	I	-----	5813. 14	1	------	I	-----
5713. 267	100	10	I	7	5816. 499	3	------	I	-----
5719. 175	600	100	I	2	5817. 475	80	6	I	3
5721. 68	3	------	I	-----	5817. 920	6	------	I	-----
5723. 880	8	1	I	-----	5818. 194	4	------	I	-----
5724. 80	6	------	I	-----	5818. 58	1	------	I	-----
5729. 683	20	2	I	-----	5837. 05	6	------	I	-----
5734. 13	10	------	I	-----	5838. 896	40	4	I	1
5734. 514	50	6	I	3?	5842. 235	20	300	II	4
5735. 61	2	------	I	-----	5844. 879	8	1	I	-----
5735. 986	9	1	I	-----	5845. 866	100	10	I	2
5736. 32	1	------	I	-----	5847. 12	3	------	I	-----
5736. 92	7	------	I	-----	5847. 768	80	8	I	2
5737. 37	1	4	II	-----	5849. 688	60	8	I	1
5738. 24	1	2	II	-----	5851. 54	1	------	I	-----
5739. 915	4	------	I	-----	5853. 44	1	------	I	-----
5740. 93	1	------	I	-----	5853. 76	3	------	I	-----
5743. 49	1	------	I	-----	5856. 55	1h	------	I	-----
5744. 217	10	1	I	-----	5858. 349	30	3	I	2
5744. 37	1	------	I	-----	5859. 07	4	------	I	-----
5745. 12	1	------	I	-----	5859. 34	3	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity: Tube	Intensity: Spark	Spectrum	Zeeman type	Wavelength in air	Intensity: Tube	Intensity: Spark	Spectrum	Zeeman type
A					*A*				
5860. 42	4	------	I	-----	5971. 91	2	------	I	-----
5862. 07	2	------	I	-----	5974. 294	200	30	I	2
5864. 32	1	------	I	-----	5974. 728	80	8	I	1
5868. 195	8	------	I	-----	5978. 67	150	20	I	7
5868. 39	2	------	I	-----	5980. 264	8	------	I	-----
5868. 50	1	------	I	-----	5981. 24	2	------	I	-----
5868. 97	2	------	I	-----	5981. 41	1	------	I	-----
5869. 106	7	------	I	-----	5983. 381	9	1	I	-----
5871. 84	1	------	I	-----	5986. 22	1	------	I	-----
5872. 93	3h	------	I	-----	5986. 62	20	2	I	1
5873. 712	7	------	I	-----	5989. 76	2	------	I	-----
5879. 772	8	------	I	-----	5991. 567	4	------	I	-----
5881. 44	1	------	I	-----	5991. 806	5	------	I	-----
5882. 50	2	------	I	-----	5991. 97	4	------	I	-----
5883. 650	70	10	I	7	5992. 08	3	------	I	-----
5885. 04	3	------	I	-----	5992. 97	50	6	I	7
5886. 31	30	2	I	3	5993. 07	5	------	I	-----
5887. 43	20	2	I	1	5994. 58	10	------	I	2
5890. 46	200	30	I	1	5996. 70	1	------	I	-----
5891. 18	5	------	I	-----	5996. 99	1	------	I	-----
5892. 80	3	------	I	-----	5998. 05	3	------	I	-----
5896. 63	50	4	I	7	6000. 56	1	------	I	-----
5898. 19	1	15Hl	II	7	6002. 30	1	------	I	-----
5900. 53	3	------	I	-----	6002. 51	1	------	I	-----
5902. 95	500	70	I	3	6002. 64	2	------	I	-----
5906. 259	4	------	I	-----	6004. 18	30	2	I	3
5906. 393	8	------	I	-----	6006. 375	2	6hl	II	4
5911. 506	4	------	I	-----	6007. 03	3	------	I	-----
5913. 91	2	------	I	-----	6011. 843	4	------	I	-----
5914. 73	1	------	I	-----	6014. 90	2	------	I	-----
5918. 28	1	------	I	-----	6015. 360	10	------	I	-----
5922. 94	10	------	I	-----	6016. 78	100	20	I	1
5926. 48	40	5	I	7	6017. 83	2	------	I	-----
5927. 208	5	------	I	-----	6018. 46	2	------	I	-----
5927. 53	2	------	I	-----	6019. 34	3	------	I	-----
5929. 36	2	15hl	II	6	6021. 77	20	2	I	2
5933. 70	150	20	I	3	6022. 54	1	------	I	-----
5936. 02	5	------	I	-----	6024. 93	2	------	I	-----
5938. 142	15	2	I	2	6026. 14	7	------	I	-----
5938. 80	1	------	I	-----	6027. 559	5	200h	II	4
5942. 41	3	------	I	-----	6030. 58	3	------	I	-----
5944. 10	1	------	I	-----	6031. 92	2	20hl	II	5
5945. 12	2	------	I	-----	6033. 938	2	------	I	-----
5945. 78	1	------	I	-----	6038. 82	3	------	I	-----
5946. 524	7	------	I	-----	6039. 711	10	1	I	-----
5949. 390	6	------	I	-----	6040. 37	15	1	I	2
5949. 60	1	------	I	-----	6041. 43	3	30hl	II	5
5949. 80	2	------	I	-----	6044. 61	1	------	I	-----
5950. 26	1	------	I	-----	6047. 98	4	15hl	II	5
5951. 24	1	------	I	-----	6048. 86	1	------	I	-----
5952. 86	2	------	I	-----	6052. 071	4	------	I	-----
5953. 13	1	------	I	-----	6054. 166	80	6	I	7
5954. 20	1h	------	I	-----	6059. 067	4	------	I	-----
5954. 71	4	------	I	-----	6059. 62	1	------	I	-----
5957. 24	4	------	I	-----	6063. 75	2	------	I	-----
5959. 30	2	------	I	-----	6064. 257	10	1	I	-----
5959. 57	5	------	I	-----	6064. 712	4	------	I	-----
5966. 30	4	------	I	-----	6069. 20	3	------	I	-----
5968. 37	1	------	I	-----	6070. 16	1	------	I	-----
5969. 37	5	20hl	II	5	6070. 591	8	1	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
5650. 811	50	6	I	3	5745. 22	2	------	I	-----
5654. 645	80	9	I	3	5748. 72	80	9	I	3
5658. 777	1	10hl	II	-----	5751. 510	3	------	I	-----
5660. 38	1	7hl	II	-----	5751. 718	4	------	I	-----
5660. 97	1	------	I	-----	5752. 18	3	------	I	-----
5662. 078	40	4	I	1	5752. 531	2	20hl	II	6
5662. 982	20	2	I	2	5756. 51	3	------	I	-----
5664. 37	------	6hl	II	-----	5756. 83	10	------	I	-----
5664. 824	4	------	I	-----	5758. 96	10	------	I	-----
5668. 716	20	2	I	2	5762. 41	2	------	I	-----
5673. 565	4	100hl	II	7	5765. 37	40	4	I	2
5677. 210	8	------	I	-----	5765. 96	30	4	I	7
5679. 553	30	------	I	2	5766. 50	------	2	II	-----
5680. 444	10	------	I	-----	5767. 20	20	60	II	6
5681. 110	4	------	I	-----	5771. 397	15	------	I	-----
5682. 34	2	------	I	-----	5773. 33	1	------	I	-----
5682. 47	1	------	I	-----	5774. 016	8	------	I	-----
5683. 738	6	------	I	7	5774. 89	3	------	I	-----
5684. 807	15	1	I	-----	5776. 00	1	------	I	-----
5686. 18	1	------	I	-----	5778. 92	1	------	I	-----
5688. 12	15	------	I	-----	5780. 46	------	7	II	-----
5688. 81	1	2	II	-----	5784. 75	2h	------	I	-----
5689. 77	1	8hl	II	-----	5791. 71	10	------	I	-----
5690. 41	1	------	I	-----	5794. 72	10	------	I	-----
5690. 58	1	------	I	-----	5796. 329	30	2	I	3?
5691. 15	1	------	I	-----	5799. 760	50	5	I	3
5691. 914	3	------	I	-----	5800. 567	4	------	I	-----
5692. 72	1	------	I	-----	5801. 693	5	70	II	7
5693. 02	4	------	I	-----	5801. 83	6	------	I	-----
5694. 34	5	------	I	-----	5802. 88	40	3	I	3
5695. 732	8	1	I	-----	5803. 64	2	------	I	-----
5697. 25	15	2	I	3	5804. 84	1	------	I	-----
5699. 46	4	------	I	-----	5806. 28	1	------	I	-----
5700. 82	1	------	I	-----	5808. 428	30	2	I	-----
5701. 11	4	------	I	-----	5809. 27	5	------	I	-----
5702. 10	20	2	I	1	5809. 499	40	100	II	6
5703. 95	2h	------	I	-----	5810. 26	2	------	I	-----
5706. 64	5	------	I	-----	5810. 58	2	------	I	-----
5706. 85	2	------	I	-----	5811. 275	15	2	I	-----
5708. 38	10	------	I	-----	5813. 14	1	------	I	-----
5713. 267	100	10	I	7	5816. 499	3	------	I	-----
5719. 175	600	100	I	2	5817. 475	80	6	I	3
5721. 68	3	------	I	-----	5817. 920	6	------	I	-----
5723. 880	8	1	I	-----	5818. 194	4	------	I	-----
5724. 80	6	------	I	-----	5818. 58	1	------	I	-----
5729. 683	20	2	I	-----	5837. 05	6	------	I	-----
5734. 13	10	------	I	-----	5838. 896	40	4	I	1
5734. 514	50	6	I	3?	5842. 235	20	300	II	4
5735. 61	2	------	I	-----	5844. 879	8	1	I	-----
5735. 986	9	1	I	-----	5845. 866	100	10	I	2
5736. 32	1	------	I	-----	5847. 12	3	------	I	-----
5736. 92	7	------	I	-----	5847. 768	80	8	I	2
5737. 37	1	4	II	-----	5849. 688	60	8	I	1
5738. 24	1	2	II	-----	5851. 54	1	------	I	-----
5739. 915	4	------	I	-----	5853. 44	1	------	I	-----
5740. 93	1	------	I	-----	5853. 76	3	------	I	-----
5743. 49	1	------	I	-----	5856. 55	1h	------	I	-----
5744. 217	10	1	I	-----	5858. 349	30	3	I	2
5744. 37	1	------	I	-----	5859. 07	4	------	I	-----
5745. 12	1	------	I	-----	5859. 34	3	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity: Tube	Intensity: Spark	Spectrum	Zeeman type
A				
5860. 42	4	------	I	-----
5862. 07	2	------	I	-----
5864. 32	1	------	I	-----
5868. 195	8	------	I	-----
5868. 39	2	------	I	-----
5868. 50	1	------	I	-----
5868. 97	2	------	I	-----
5869. 106	7	------	I	-----
5871. 84	1	------	I	-----
5872. 93	3h	------	I	-----
5873. 712	7	------	I	-----
5879. 772	8	------	I	-----
5881. 44	1	------	I	-----
5882. 50	2	------	I	-----
5883. 650	70	10	I	7
5885. 04	3	------	I	-----
5886. 31	30	2	I	3
5887. 43	20	2	I	1
5890. 46	200	30	I	1
5891. 18	5	------	I	-----
5892. 80	3	------	I	-----
5896. 63	50	4	I	7
5898. 19	1	15Hl	II	7
5900. 53	3	------	I	-----
5902. 95	500	70	I	3
5906. 259	4	------	I	-----
5906. 393	8	------	I	-----
5911. 506	4	------	I	-----
5913. 91	2	------	I	-----
5914. 73	1	------	I	-----
5918. 28	1	------	I	-----
5922. 94	10	------	I	-----
5926. 48	40	5	I	7
5927. 208	5	------	I	-----
5927. 53	2	------	I	-----
5929. 36	2	15hl	II	6
5933. 70	150	20	I	3
5936. 02	5	------	I	-----
5938. 142	15	2	I	2
5938. 80	1	------	I	-----
5942. 41	3	------	I	-----
5944. 10	1	------	I	-----
5945. 12	2	------	I	-----
5945. 78	1	------	I	-----
5946. 524	7	------	I	-----
5949. 390	6	------	I	-----
5949. 60	1	------	I	-----
5949. 80	2	------	I	-----
5950. 26	1	------	I	-----
5951. 24	1	------	I	-----
5952. 86	2	------	I	-----
5953. 13	1	------	I	-----
5954. 20	1h	------	I	-----
5954. 71	4	------	I	-----
5957. 24	4	------	I	-----
5959. 30	2	------	I	-----
5959. 57	5	------	I	-----
5966. 30	4	------	I	-----
5968. 37	1	------	I	-----
5969. 37	5	20hl	II	5
A				
5971. 91	2	------	I	-----
5974. 294	200	30	I	2
5974. 728	80	8	I	1
5978. 67	150	20	I	7
5980. 264	8	------	I	-----
5981. 24	2	------	I	-----
5981. 41	1	------	I	-----
5983. 381	9	1	I	-----
5986. 22	1	------	I	-----
5986. 62	20	2	I	1
5989. 76	2	------	I	-----
5991. 567	4	------	I	-----
5991. 806	5	------	I	-----
5991. 97	4	------	I	-----
5992. 08	3	------	I	-----
5992. 97	50	6	I	7
5993. 07	5	------	I	-----
5994. 58	10	------	I	2
5996. 70	1	------	I	-----
5996. 99	1	------	I	-----
5998. 05	3	------	I	-----
6000. 56	1	------	I	-----
6002. 30	1	------	I	-----
6002. 51	1	------	I	-----
6002. 64	2	------	I	-----
6004. 18	30	2	I	3
6006. 375	2	6hl	II	4
6007. 03	3	------	I	-----
6011. 843	4	------	I	-----
6014. 90	2	------	I	-----
6015. 360	10	------	I	-----
6016. 78	100	20	I	1
6017. 83	2	------	I	-----
6018. 46	2	------	I	-----
6019. 34	3	------	I	-----
6021. 77	20	2	I	2
6022. 54	1	------	I	-----
6024. 93	2	------	I	-----
6026. 14	7	------	I	-----
6027. 559	5	200h	II	4
6030. 58	3	------	I	-----
6031. 92	2	20hl	II	5
6033. 938	2	------	I	-----
6038. 82	3	------	I	-----
6039. 711	10	1	I	-----
6040. 37	15	1	I	2
6041. 43	3	30hl	II	5
6044. 61	1	------	I	-----
6047. 98	4	15hl	II	5
6048. 86	1	------	I	-----
6052. 071	4	------	I	-----
6054. 166	80	6	I	7
6059. 067	4	------	I	-----
6059. 62	1	------	I	-----
6063. 75	2	------	I	-----
6064. 257	10	1	I	-----
6064. 712	4	------	I	-----
6069. 20	3	------	I	-----
6070. 16	1	------	I	-----
6070. 591	8	1	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum		Zeeman type
	Tube	Spark			
A					
6071. 92	2	------	I		-----
6073. 50	1	------	I		-----
6074. 360	10	------	I		-----
6075. 50	1	------	I		-----
6077. 53	2h	------	I		-----
6079. 59	1	------	I		-----
6084. 67	1	------	I		-----
6085. 71	3	------	I		-----
6090. 80	4	------	I		1
6091. 37	20	2	I		
6092. 44	8	------	I		-----
6092. 90	2	------	I		-----
6093. 14	2	20hl		II	7
6094. 88	4	------	I		-----
6097. 47	------	10Hl		II	4
6098. 68	200	30	I		3
6104. 58	20	3	I		2
6104. 88	15	2	I		-----
6105. 07	3	------	I		-----
6106. 11	10	1	I		-----
6106. 22	2	------	I		-----
6108. 90	1	------	I		-----
6109. 22	1	------	I		-----
6115. 29	3	------	I		-----
6116. 62	5	------	I		-----
6118. 16	40	6	I		1
6119. 27	2	------	I		-----
6119. 70	5	------	I		-----
6122. 00	15	2	I		-----
6122. 93	3	------	I		-----
6126. 30	6	------	I		-----
6128. 14	3	------	I		-----
6129. 19	1	------	I		-----
6129. 49	1	------	I		-----
6135. 10	10	200hl		II	4
6135. 40	10	------	I		-----
6135. 68	3	6		II	-----
6138. 51	2	------	I		-----
6138. 73	1	------	I		-----
6139. 00	3	------	I		-----
6140. 46	2	------	I		-----
6141. 78	3	------	I		-----
6142. 15	2	------	I		-----
6142. 77	1	------	I		-----
6144. 392	30	2	I		1
6144. 58	20	------	I		-----
6146. 54	5	------	I		-----
6146. 99	3	------	I		-----
6147. 24	3	------	I		-----
6148. 68	7	1	I		-----
6150. 01	3	------	I		-----
6152. 952	10	1	I		1
6156. 264	3	20hl		II	5
6156. 54	------	4hl		II	-----
6158. 76	------	20hl		II	6
6160. 681	------	30hl		II	6
6164. 70	2	------	I		-----
6166. 59	1	------	I		-----
6167. 04	10	------	I		-----
6168. 03	3	------	I		-----
A					
6168. 66	20	2	I		2
6172. 74	1	------	I		-----
6173. 89	------	4hl		II	-----
6176. 55	3	------	I		-----
6176. 99	2	------	I		-----
6185. 128	400	40	I		3
6189. 21	------	8Hl		II	-----
6191. 33	1	------	I		-----
6191. 784	10	------	I		-----
6192. 475	50	5	I		2
6193. 806	4	------	I		-----
6198. 460	20	2	I		2
6200. 890	4	------	I		-----
6202. 86	3	10		II	4
6206. 36	10	------	I		-----
6206. 51	12	------	I		-----
6206. 926	1	30hl		II	4
6207. 08	1	------	I		-----
6207. 46	10	1	I		-----
6207. 97	10	1	I		-----
6209. 43	40	4	I		2
6210. 680	150	20	I		2
6211. 21	1	10Hl		II	-----
6211. 60	4	------	I		-----
6211. 70	3	------	I		-----
6212. 00	20	2	I		2
6212. 71	1	------	I		7
6216. 800	80	10	I		-----
6217. 315	1	10		II	-----
6219. 83	1	------	I		-----
6222. 81	10	40hl		II	6
6223. 74	1	------	I		-----
6224. 35	2	------	I		-----
6227. 03	2	------	I		-----
6228. 20	------	2		II	-----
6229. 10	15	1	I		-----
6229. 63	1	20hl		II	-----
6230. 825	6	60hl		II	5
6236. 51	8	2	I		-----
6237. 34	3	------	I		-----
6238. 59	100	10	I		3
6241. 81	10	1	I		7
6242. 27	7	------	I		-----
6243. 83	1	------	I		-----
6248. 94	50	200		II	5
6250. 16	1	------	I		-----
6250. 36	2	------	I		-----
6252. 92	1	------	I		-----
6256. 97	70	9	I		1
6258. 79	40	4	I		2
6262. 71	1	------	I		-----
6262. 94	3	------	I		-----
6266. 63	1	------	I		-----
6270. 44	2	------	I		-----
6271. 06	3	15hl		II	-----
6271. 355	15	2	I		-----
6272. 770	9	1	I		-----
6273. 25	1	------	I		-----
6275. 49	15	------	I		-----
6276. 41	3	------	I		-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity: Tube	Intensity: Spark	Spectrum	Zeeman type
A				
6277.197	10	1	I	7
6278.40	1	------	I	-----
6278.804	4	------	I	-----
6279.834	15	60	II	6
6290.10	1	------	I	-----
6296.27	5	------	I	-----
6297.903	4	------	I	-----
6298.12	3	------	I	-----
6298.63	1	------	I	-----
6299.52	50	6	I	1
6299.99	8	------	I	-----
6300.128	20	------	I	-----
6300.72	8	------	I	-----
6300.94	2	------	I	-----
6302.63	1	------	I	-----
6303.16	2	------	I	-----
6303.90	1	------	I	-----
6304.31	1	------	I	-----
6306.00	3	------	I	-----
6306.201	1	15Hl	II	4
6306.50	2	------	I	-----
6307.91	1	------	I	-----
6309.67	1	------	I	-----
6310.74	10	1	I	-----
6311.844	50	7	I	3
6312.72	3	------	I	-----
6313.41	30	2	I	-----
6315.92	2	30hl	II	5
6318.313	30	3	I	1
6323.69	1	------	I	-----
6328.51	3	------	I	-----
6328.76	1	------	I	-----
6330.66	3	------	I	-----
6337.74	------	2	II	-----
6338.096	80	9	I	1
6340.24	3	------	I	-----
6340.48	3	------	I	-----
6340.708	15	2	I	-----
6343.742	1	8hl	II	-----
6343.98	2	------	I	-----
6345.08	3	------	I	-----
6347.10	8	------	I	-----
6347.37	2	------	I	-----
6347.63	5	------	I	-----
6349.91	4	------	I	-----
6353.46	3	------	I	-----
6354.30	1	------	I	-----
6355.393	5	------	I	-----
6355.68	4	------	I	-----
6355.99	1	------	I	-----
6357.47	1	------	I	-----
6359.84	10	1	I	-----
6363.08	1	------	I	-----
6366.87	1	------	I	-----
6367.09	3	------	I	-----
6370.018	10	1	I	-----
6371.36	4	------	I	-----
6372.792	2	------	I	-----
6373.46	1	------	I	-----
6375.03	1	------	I	-----

Wavelength in air	Intensity: Tube	Intensity: Spark	Spectrum	Zeeman type
A				
6376.19	20	2	I	3
6376.88	1	------	I	-----
6377.53	3	------	I	-----
63806.19	80	7	I	3
6381.564	10	------	I	-----
6382.232	10	------	I	-----
6383.69	20	1	I	-----
6386.229	300	40	I	2
6388.914	20	2	I	3
6390.22	10	------	I	-----
6390.40	2	------	I	-----
6396.67	1	------	I	-----
6397.91	1	------	I	-----
6398.94	1	------	I	-----
6400.24	2	------	I	-----
6406.53	15	------	I	-----
6409.50	70	7	I	4?
6418.02	10	------	I	7
6420.58	1	------	I	-----
6420.86	1	------	I	-----
6421.10	6	------	I	-----
6421.91	2	------	I	-----
6422.76	1	------	I	-----
6423.40	5	------	I	-----
6429.44	10	------	I	3
6430.75	5	------	I	-----
6431.46	1	------	I	-----
6434.52	2	------	I	-----
6434.77	4	------	I	-----
6435.60	1	------	I	-----
6436.99	6	------	I	-----
6438.36	1	------	I	-----
6439.03	1	------	I	-----
6442.22	1	------	I	-----
6443.11	1	------	I	-----
6444.07	5	------	I	-----
6447.10	1	------	I	-----
6449.166	4	------	I	-----
6449.52	2	------	I	-----
6451.16	1	------	I	-----
6454.466	3	------	I	-----
6455.84	2	15hl	II	-----
6456.956	50	6	I	3
6461.49	1	------	I	-----
6462.28	2	4	II	4
6466.59	1	------	I	-----
6467.931	8	------	I	-----
6468.32	4	------	I	-----
6469.324	3	------	I	-----
6472.14	1	------	I	-----
6472.67	6	------	I	-----
6473.882	3	20hl	II	4
6474.14	4	------	I	-----
6475.04	1	------	I	-----
6477.03	4	------	I	-----
6478.72	1	------	I	-----
6479.486	7	------	I	-----
6481.55	4	------	I	-----
6482.526	3	------	I	-----
6483.32	1	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
6485. 43	3	------	I	-----	6584. 53	4	100hl	II	4
6486. 32	1	------	I	-----	6585. 794	8	------	I	----
6490. 61	2	------	I	-----	6587. 23	150	15	I	3
6492. 54	5	------	I	-----	6590. 111	10	1	I	----
6494. 589	1	5	II	-----	6590. 54	1	------	I	----
6495. 64	1	------	I	-----	6590. 767	8	1	I	----
6498. 46	1	------	I	-----	6591. 80	30	1	I	----
6500. 49	4	------	I	-----	6595. 188	2	------	I	----
6501. 85	1	------	I	-----	6595. 491	8	------	I	----
6505. 12	1	------	I	-----	6596. 654	6	------	I	----
6505. 22	1	------	I	-----	6596. 90	2	------	I	----
6507. 12	4	------	I	-----	6599. 766	2	4	II	----
6508. 12	5	------	I	-----	6605. 91	------	3	II	----
6510. 388	6	------	I	-----	6609. 20	1	8	II	6
6511. 61	1	8hl	II	-----	6611. 02	1	------	I	----
6511. 81	3h	------	I	-----	6612. 68	2	------	I	----
6512. 37	3	------	I	-----	6616. 18	5	------	I	----
6512. 61	2	8	II	4	6616. 66	4	------	I	----
6518. 14	1	------	I	---	6621. 13	1	------	I	----
6519. 82	1	------	I	-----	6622. 76	2	------	I	----
6521. 175	15	1	I	-----	6624. 35	1	------	I	----
6521. 82	2	------	I	-----	6625. 57	4	------	I	----
6523. 92	30	2	I	3	6626. 62	3	------	I	----
6525. 13	2	------	I	-----	6627. 91	2	------	I	----
6525. 330	2	------	I	-----	6628. 767	6	------	I	----
6525. 66	1	------	I	-----	6632. 59	2	------	I	----
6526. 03	3	------	I	-----	6633. 52	1	------	I	----
6526. 183	1	8Hl	II	-----	6639. 97	2	------	I	----
6526. 77	9	------	I	-----	6641. 21	2	------	I	----
6527. 05	1	------	I	-----	6643. 085	9	------	I	----
6530. 23	3	------	I	-----	6644. 609	100	300	II	7
6531. 66	4	20	II	5	6646. 15	1	------	I	----
6531. 86	10	------	I	-----	6647. 04	40	200	II	7
6534. 09	4	------	I	-----	6649. 05	2	------	I	----
6536. 56	15	------	I	1	6654. 52	1	------	I	----
6540. 24	2	------	I	-----	6656. 76	1	------	I	----
6541. 58	2	------	I	-----	6657. 51	9	------	I	----
6542. 82	2	40hl	II	7	6659. 42	40	4	I	3
6546. 02	------	2	II	-----	6660. 507	1	------	I	----
6548. 24	2	20Hl	II	6	6663. 90	2	------	I	----
6549. 35	1	------	I	-----	6664. 64	1	------	I	----
6549. 99	1	20hl	II	-----	6665. 839	1	------	I	----
6550. 68	9	------	I	-----	6666. 35	10	------	I	----
6552. 91	20	2	I	2	6667. 89	3hl	------	I	----
6556. 48	70	6	I	1	6668. 14	4h	------	I	----
6557. 59	4	------	I	-----	6669. 34	15	2	I	1
6557. 91	10	60hl	II	6	6669. 49	2	------	I	----
6562. 83	1	6	II	6	6669. 97	2	------	I	----
6565. 75	1	4	II	-----	6670. 47	1	------	I	----
6567. 39	4	60hl	II	4	6671. 28	20	2	I	2
6567. 67	20	------	I	-----	6676. 39	5	------	I	----
6568. 02	3	------	I	-----	6678. 82	6	1	I	----
6572. 27	5	------	I	-----	6684. 50	30	2	I	3
6573. 48	1	------	I	-----	6691. 66	20	2	I	----
6573. 78	2	------	I	-----	6693. 491	15	1	I	1
6576. 964	4	------	I	-----	6694. 26	2	------	I	----
6578. 138	4	------	I	-----	6698. 45	2	------	I	----
6582. 14	1	------	I	-----	6702. 30	1	------	I	----
6583. 26	3	------	I	-----	6702. 90	3	------	I	----
6584. 42	2	------	I	-----	6704. 17	2	------	I	----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
6704. 33	2	------	I	-----	6839. 378	1	------	I	-----
6704. 926	4	------	I	-----	6841. 182	9	1	I	-----
6705. 23	4	------	I	-----	6849. 22	10	------	I	-----
6705. 740	1	------	I	-----	6849. 57	1	------	I	-----
6707. 032	1	------	I	-----	6850. 06	60	8	I	1
6707. 200	4	------	I	-----	6851. 314	9	------	I	-----
6707. 662	2	------	I	-----	6852. 24	3	------	I	-----
6708. 33	20	3	I	7	6852. 906	10	1	I	-----
6709. 39	3	50hl	II	6	6853. 01	2	------	I	-----
6713. 48	200	20	I	1	6855. 29	10	40	II	5
6716. 014	30	3	I	2	6857. 03	20	3	I	7
6717. 19	3	------	I	-----	6858. 56	60	10	I	-----
6718. 87	2	------	I	-----	6858. 76	200	40	I	1
6720. 95	2	------	I	-----	6860. 45	4	------	I	-----
6723. 51	3	------	I	-----	6861. 26	1	------	I	-----
6734. 65	2	------	I	-----	6862. 77	1	------	I	-----
6736. 42	1	------	I	-----	6865. 96	1	------	I	-----
6737. 15	1	------	I	-----	6869. 32	1	------	I	-----
6739. 210	9	1	I	-----	6874. 89	40	5	I	2
6742. 64	1	------	I	-----	6884. 53	10	1	I	-----
6744. 00	7	------	I	-----	6889. 81	10	1	I	-----
6745. 61	1	------	I	-----	6896. 52	15	2	I	-----
6747. 00	2	------	I	-----	6902. 78	12	1	I	-----
6747. 16	1	------	I	-----	6911. 40	300	80	I	1
6747. 56	1	------	I	-----	6914. 17	5	------	I	-----
6749. 15	1	------	I	-----	6917. 48	4	------	I	-----
6751. 47	1	3	II	-----	6926. 21	70	10	I	0
6754. 624	70	200	II	5	6926. 780	15	------	I	-----
6756. 16	2	------	I	-----	6928. 15	2	------	I	-----
6762. 42	4	------	I	-----	6935. 16	8	30	II	-----
6763. 03	1	------	I	-----	6936. 57	3	------	I	-----
6763. 705	9	1	I	-----	6937. 456	7	1	I	-----
6767. 27	20	2	I	-----	6938. 85	1	------	I	-----
6767. 88	5	------	I	-----	6947. 53	20	2	I	-----
6769. 924	40	5	I	3	6949. 24	1	------	I	-----
6770. 87	2h	------	I	-----	6952. 849	12	1	I	-----
6773. 06	30	3	I	3?	6954. 17	20	2	I	-----
6773. 63	3h	------	I	-----	6956. 80	3	------	I	-----
6774. 22	2	------	I	-----	6962. 46	1	------	I	-----
6774. 36	4	------	I	-----	6965. 809	40	5	I	-----
6778. 24	1	------	I	-----	6967. 71	1	------	I	-----
6782. 66	1	------	I	-----	6970. 42	50	6	I	-----
6786. 40	1	------	I	-----	6972. 03	4	------	I	-----
6789. 28	1000	100	I	2	6972. 53	2	------	I	-----
6793. 99	10	------	I	-----	6973. 03	1	------	I	-----
6797. 56	2	------	I	-----	6976. 20	20	2	I	-----
6797. 810	3	------	I	-----	6978. 30	1	------	I	-----
6798. 481	1	------	I	-----	6979. 61	100	20	I	3?
6801. 771	7	1	I	-----	6980. 905	100	200	II	7
6805. 313	3	------	I	-----	6981. 61	50	8	I	-----
6814. 96	5	------	I	-----	6982. 75	1	------	I	-----
6818. 95	2000	300	I	1	6997. 84	2	10	II	-----
6822. 06	4	------	I	-----	7002. 94	10	1	I	-----
6824. 34	3	------	I	-----	7007. 36	2	------	I	-----
6826. 55	100	10	I	7	7010. 69	30	4	I	-----
6832. 62	3h	------	I	-----	7014. 29	20	2	I	-----
6833. 750	20	2	I	7?	7016. 99	------	6	II	-----
6834. 18	1	------	I	-----	7018. 22	3	------	I	-----
6836. 83	1	------	I	-----	7019. 25	50	10	I	-----
6837. 95	4	------	I	-----	7021. 23	6	20	II	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark		
A				
7026. 24	1	------	I	-----
7028. 24	1	------	I	-----
7028. 52	1	------	I	-----
7028. 93	3	------	I	-----
7030. 31	50	100	II	6
7032. 55	12	1	I	-----
7035. 15	70	10	I	-----
7036. 48	2	------	I	-----
7036. 95	5	------	I	-----
7038. 07	2	------	I	-----
7039. 16	12	1	I	-----
7040. 54	1	------	I	-----
7042. 69	3	------	I	-----
7046. 35	2	------	I	-----
7048. 885	12	1	I	-----
7049. 72	6	------	I	-----
7050. 11	1	------	I	-----
7052. 65	50	6	I	-----
7054. 052	40	4	I	-----
7054. 515	4	------	I	-----
7055. 38	5	------	I	-----
7061. 90	80	10	I	-----
7062. 85	150	20	I	-----
7063. 852	3000	400	I	-----
7064. 34	15?	30?	I II	3
7065. 83	12	2	I	-----
7070. 77	6	1	I	-----
7071. 01	2	------	I	-----
7074. 76	2	------	I	-----
7075. 34	1	------	I	-----
7081. 28	1	------	I	-----
7083. 016	6	------	I	-----
7084. 61	4	------	I	-----
7085. 02	2	------	I	-----
7085. 33	6	------	I	-----
7086. 71	6	------	I	-----
7089. 81	7	------	I	-----
7093. 83	50	6	I	-----
7094. 412	100	15	I	-----
7096. 15	5	------	I	3?
7096. 36	15	2	I	-----
7096. 712	12	1	I	-----
7100. 546	150	20	I	-----
7105. 28	2	------	I	-----
7114. 46	2	------	I	-----
7114. 85	3	------	I	-----
7115. 685	40	7	I	-----
7118. 37	30	5	I	-----
7119. 520	700	100	I	-----
7120. 80	30	5	I	1
7131. 82	7000	1000	I	-----
7144. 81	4	------	I	2
7153. 21	6	1	I	-----
7156. 31	10	2	I	-----
7156. 93	1	------	I	-----
7157. 945	30	4	I	-----
7161. 19	1	------	I	-----
7161. 64	2	------	I	-----
7162. 643	7	1	I	-----
7163. 48	3	------	I	-----
7163. 58	1	------	I	-----
7164. 52	4	10	II	-----
7167. 42	10	2	I	-----
7175. 94	1	------	I	-----
7177. 12	8	1	I	-----
7179. 20	3	------	I	-----
7181. 148	6	1	I	-----
7182. 94	3	------	I	-----
7185. 985	40	6	I	-----
7188. 84	3	------	I	-----
7189. 31	5	10	II	-----
7189. 99	1	------	I	-----
7191. 21	3	------	I	-----
7196. 09	20	5	I	-----
7200. 91	12	1	I	-----
7204. 684	4	------	I	-----
7205. 08	30	5	I	-----
7206. 31	1	------	I	-----
7212. 882	2	------	I	-----
7216. 53	12	1	I	-----
7220. 76	7	------	I	-----
7221. 20	2	------	I	-----
7221. 86	8	1	I	-----
7222. 64	20	3	I	-----
7223. 01	1	------	I	-----
7225. 15	1	------	I	-----
7231. 565	30	4	I	-----
7233. 10	15	2	I	-----
7237. 101	8000	1000	I	-----
7240. 87	5000	600	I	1
7244. 11	40	5	I	1
7251. 66	5	------	I	-----
7251. 80	2	------	I	-----
7255. 43	5	1	I	-----
7257. 99	5	------	I	-----
7261. 82	4	------	I	-----
7262. 587	80	10	I	-----
7263. 04	15	2	I	3
7271. 24	2	------	I	-----
7272. 33	1	------	I	-----
7272. 93	1	------	I	-----
7273. 28	7	1	I	-----
7277. 07	5	------	I	-----
7277. 64	20	50	II	-----
7277. 90	15	2	I	-----
7278. 74	1	4	II	-----
7280. 006	10	2	I	-----
7281. 52	30	5	I	-----
7282. 01	1	------	I	-----
7282. 29	3	------	I	-----
7283. 43	1	------	I	-----
7285. 12	2	------	I	-----
7285. 58	1	------	I	-----
7287. 79	1	------	I	-----
7288. 31	1	------	I	-----
7290. 13	1	------	I	-----
7292. 29	2	5	II	-----
7294. 026	20	4	I	-----
7294. 31	10	1	I	-----
7294. 98	3	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
7297.06	1	------	I	-----	7430.09	4	------	I	-----
7297.33	2	------	I	-----	7437.600	500	100	I	3
7298.79	3	------	I	-----	7441.16	6	------	I	-----
7301.03	5	1	I	-----	7444.26	20	3?	I	-----
7303.63	15	2	I	-----	7444.81	12	1?	I	-----
7309.38	5	------	I	-----	7447.19	3	------	I	-----
7312.68	1	2	II?	-----	7447.39	1	------	I	-----
7315.25	10	1	I	-----	7447.724	5	------	I	-----
7315.72	1	2	II?	-----	7448.66	7	------	I	-----
7316.94	2	------	I	-----	7450.59	1	------	I	-----
7320.06	1000	200	I	7	7451.94	6	------	I	-----
7321.79	150	30	I	1	7461.30	10	1	I	-----
7322.91	15	2	I	-----	7462.51	3	------	I	-----
7323.43	3h	------	I	-----	7463.905	200	40	I	7
7324.13	2	------	I	-----	7473.67	6	------	I	-----
7327.175	15	2	I	-----	7476.53	2	------	I	-----
7328.63	15	30	II	-----	7476.71	4	------	I	-----
7334.73	1	------	I	-----	7479.78	15	2	I	-----
7334.88	2	3	I II?	-----	7480.781	20	2	I	-----
7337.93	12	2	I	-----	7483.704	4	------	I	-----
7339.294	40	7	I	-----	7484.603	50	10	I	-----
7342.01	1	------	I	-----	7488.17	30	4	I	-----
7342.80	1	------	I	-----	7489.02	15	2	I	-----
7344.70	2	------	I	-----	7492.11	10	1	I	-----
7346.14	3h	------	I	-----	7501.63	1	------	I	-----
7352.41	1	------	I	-----	7506.80	3	------	I	-----
7356.18	100	15	I	-----	7508.77	2	------	I	-----
7358.78	3	------	I	-----	7511.00	10?	------	I	-----
7359.916	3	------	I	-----	7511.47	1	------	I	-----
7365.35	100	20	I	-----	7513.36	2	------	I	-----
7368.160	30	6	I	-----	7514.98	3	5	II	-----
7374.389	15	2	I	-----	7515.22	3	------	I	-----
7375.59	1	------	I	-----	7516.79	2	------	I	-----
7376.987	4	------	I	-----	7517.49	1	------	I	-----
7377.176	8	1	I	-----	7520.38	3	------	I	-----
7378.91	2	------	I	-----	7525.09	2	------	I	-----
7381.77	1	------	I	-----	7526.82	15	2	I	-----
7384.03	10	------	I	-----	7529.21	2	------	I	-----
7384.75	1	------	I	-----	7530.13	5h	------	I	-----
7385.35	3	------	I	-----	7532.42	1	------	I	-----
7388.86	4	------	I	-----	7532.88	5	------	I	-----
7390.729	400	60	I	3	7534.81	1	------	I	-----
7392.86	4	------	I	-----	7535.11	2	------	I	-----
7396.99	15	2	I	-----	7537.35	3	------	I	-----
7398.137	12	2	I	-----	7542.39	10	1	I	-----
7398.97	3	------	I	-----	7543.40	50	6	I	-----
7400.72	12	2	I	-----	7544.81	3	------	I	-----
7402.75	15	1	I	-----	7551.64	7	1	I	-----
7408.97	30	6	I	-----	7556.37	200	40	I	2
7409.505	70	12	I	-----	7557.78	1	------	I	-----
7412.70	5	------	I	-----	7558.63	1	------	I	-----
7414.63	20	2	I	-----	7561.12	1	10	II	-----
7417.51	8	1	I	-----	7562.93	1500	300	I	1
7420.48	3	------	I	-----	7564.24	200	40	I	7
7420.76	1	------	I	-----	7565.35	------	2	II	-----
7422.416	15	2	I	-----	7568.85	2	------	I	-----
7423.628	120	20	I	3	7570.90	1	2	II	-----
7424.274	10	------	I	-----	7576.67	40	6	I	-----
7426.67	3	------	I	-----	7577.02	300	40	I	1
7427.77	1	------	I	-----	7581.18	4	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
7582. 462	70	12	I	.....	7750. 15	2	.....	I	.....
7584. 93	1	.....	I	.....	7757. 89	40	100	II	6
7586. 26	8	1	I	.....	7758. 84	1	.....	I	.....
7586. 80	1	.....	I	.....	7762. 38	15	2	I	.....
7589. 67	3	.....	I	.....	7773. 09	10	1	I	.....
7592. 977	150	30	I	1?	7773. 95	2	.....	I	.....
7599. 56	40	8	I	.....	7774. 39	5	.....	I	.....
7605. 27	3	.....	I	.....	7776. 65	3	.....	I	.....
7606. 03	2	.....	I	.....	7777. 43	10	1	I	.....
7606. 39	8	1	I	.....	7782. 56	1	.....	I	.....
7608. 549	200	40	I	.....	7783. 88	6	1	I	.....
7612. 60	50	8	I	.....	7789. 52	15	2	I	.....
7624. 387	5000	1000	I	1	7790. 90	500	100	I	2
7634. 44	10?	20?	II	.....	7796. 82	60	10	I	.....
7645. 655	400	80	I	3	7801. 54	20	60	II	4
7646. 34	20	.....	I	.....	7803. 97	4	.....	I	.....
7648. 84	4	.....	I	.....	7804. 56	2	.....	I	.....
7650. 39	2	.....	I	.....	7813. 50	10	1	I	.....
7653. 88	4h	.....	I	.....	7814. 57	400	80	I	1
7654. 99	1	.....	I	.....	7826. 62	4	.....	I	.....
7656. 39	20	4	I	.....	7830. 08	1	.....	I	.....
7660. 318	6	1	I	.....	7830. 60	5	.....	I	.....
7662. 32	2	.....	I	.....	7831. 81	8	1	I	.....
7662. 52	4	.....	I	.....	7845. 37	4000	800	I	2
7663. 09	20	50	II	7	7846. 57	50	8	I	.....
7663. 51	5h	.....	I	.....	7853. 81	12	2	I	.....
7664. 465	20	2	I	.....	7857. 78	3h	.....	I	.....
7664. 749	8	1	I	.....	7858. 32	1	.....	I	.....
7666. 09	6	.....	I	.....	7858. 52	3	.....	I	.....
7668. 414	20	2	I	.....	7861. 23	30	60	II	.....
7670. 76	1	.....	I	.....	7862. 78	60	15	I	.....
7670. 93	3	.....	I	.....	7866. 58	5	.....	I	.....
7671. 92	20	4	I	.....	7867. 26	20	4	I	.....
7676. 53	1	.....	I	.....	7870. 84	1	.....	I	.....
7678. 60	3	.....	I	.....	7877. 69	20	4	I	.....
7679. 95	3	.....	I	.....	7881. 12	1	.....	I	.....
7682. 16	2	.....	I	.....	7884. 58	3	.....	I	.....
7684. 47	1	.....	I	.....	7885. 53	4	.....	I	.....
7685. 38	2	.....	I	.....	7888. 01	7	1	I	.....
7685. 91	1	.....	I	.....	7888. 54	20	2	I	
7693. 40	4	.....	I	.....	7893. 03	4	.....	I	.....
7694. 10	12	2	I	.....	7893. 75	30	5	I	.....
7697. 38	1	.....	I	.....	7894. 01	8?	1	I	.....
7699. 37	2	3	I, II?	.....	7901. 45	8	1	I	.....
7701. 69	3	.....	I	.....	7906. 12	15	2	I	.....
7702. 171	8	.....	I	.....	7907. 17	1	.....	I	.....
7704. 530	30	2	I	.....	7908. 09	2	.....	I	.....
7706. 90	5	.....	I	.....	7908. 58	1	.....	I	.....
7709. 92	1	.....	I	.....	7910. 71	2	.....	I	.....
7710. 25	1	.....	I	.....	7911. 94	1	.....	I	.....
7714. 92	1	.....	I	.....	7914. 77	4	.....	I	.....
7717. 84	2	.....	I	.....	7917. 36	5	.....	I	.....
7720. 65	2	5	II	.....	7920. 75	2000	400	I	7
7723. 68	2	.....	I	.....	7924. 08	5	.....	I	.....
7725. 12	1	.....	I	.....	7927. 19	2	.....	I	.....
7736. 89	10?	1	I	.....	7929. 10	1	.....	I	.....
7740. 17	2000	400	I	1	7930. 04	2	.....	I	.....
7741. 59	50	10	I	.....	7930. 77	1	.....	I	.....
7743. 57	150	20	I	3	7934. 70	1	.....	I	.....
7749. 62	4	.....	I	.....	7938. 06	500	100	I	2

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
7940. 57	2	------	I	-----	8146. 05	5	------	I	-----
7940. 96	3	------	I	-----	8147. 19	2	------	I	-----
7948. 63	20	2	I	-----	8151. 54	1	------	I	-----
7950. 43	5	1	I	-----	8154. 58	1	------	I	-----
7951. 00	20	4	I	-----	8157. 59	6	------	I	-----
7951. 73	3	------	I	-----	8162. 04	3	------	I	-----
7952. 83	4	------	I	-----	8163. 60	20	2	I	-----
7954. 27	15	2	I	-----	8164. 96	1	------	I	-----
7955. 21	30	7	I	-----	8173. 90	300	70	I	1
7957. 56	4	------	I	-----	8174. 92	30	4	I	-----
7960. 31	4	------	I	-----	8176. 39	1	------	I	-----
7970. 22	1	------	I	-----	8177. 25	1h	------	I	-----
7971. 57	20	4	I	-----	8182. 02	1	------	I	-----
7972. 29	1	------	I	-----	8182. 28	1	------	I	-----
7976. 81	40	5	I	-----	8185. 72	4	------	I	-----
7976. 95	10	1	I	-----	8193. 82	100	10	I	-----
7979. 17	2	------	I	-----	8196. 61	1	------	I	-----
7980. 01	8	1	I	-----	8202. 05	6	------	I	-----
7980. 54	1	------	I	-----	8204. 57	2000	500	I	7
7983. 64	6	15	II	-----	8210. 70	1	2	II?	-----
7986. 90	40	4	I	-----	8212. 15	10	2	I	-----
7990. 03	3	------	I	-----	8217. 36	15	------	I	-----
7994. 76	5000	800	I	1	8222. 46	20	------	I	-----
8002. 44	15	1	I	-----	8224. 31	1	------	I	-----
8007. 66	1	------	I	-----	8224. 59	1	------	I	-----
8008. 68	8	1	I	-----	8226. 54	1	------	I	-----
8010. 58	100	15	I	-----	8236. 12	40	80	II	-----
8032. 24	8	1	I	-----	8238. 65	20	2	I	-----
8034. 52	1	------	I	-----	8244. 40	40	5	I	-----
8047. 26	8	1	I	-----	8248. 81	100	10	I	-----
8048. 82	4	------	I	-----	8250. 58	1	------	I	-----
8056. 47	400	80	I	-----	8251. 15	8	------	I	-----
8063. 63	1	------	I	-----	8251. 73	10	------	I	-----
8068. 34	3	------	I	-----	8254. 57	2	------	I	-----
8074. 30	1	------	I	-----	8257. 75	1	------	I	-----
8076. 83	1	------	I	-----	8264. 53	1	------	I	-----
8080. 26	500	100	I	3	8267. 38	1	------	I	-----
8080. 77	50	10	I	-----	8269. 33	1	------	I	-----
8080. 96	100	20	I	-----	8274. 29	5	------	I	-----
8082. 62	10	2	I	-----	8276. 94	1000	200	I	2
8085. 36	20?	------	I	-----	8284. 30	6h	4	I II?	-----
8085. 73	15	2	I	-----	8284. 93	7	1	I	-----
8087. 51	1	------	I	-----	8292. 00	15	2	I	-----
8091. 02	3	------	I	-----	8293. 41	20	3	I	-----
8092. 58	1	------	I	-----	8294. 70	4	------	I	-----
8092. 91	20	4	I	-----	8297. 37	1h	2	II?	-----
8094. 14	8	1	I	-----	8301. 85	4	------	I	-----
8096. 44	1	2	II	-----	8305. 33	6	------	I	-----
8103. 67	20	4	I	-----	8311. 32	1	------	I	-----
8105. 36	10	2	I	-----	8316. 35	1	------	I	-----
8106. 04	2	------	I	-----	8316. 69	1	------	I	-----
8107. 66	4	------	I	-----	8317. 60	2	------	I	-----
8118. 20	10	1	I	-----	8318. 34	1	------	I	-----
8121. 18	5	------	I	-----	8321. 35	2	------	I	-----
8128. 91	10	1	I	-----	8325. 80	1	------	I	-----
8136. 01	1	------	I	-----	8328. 97	6?	------	I	-----
8136. 63	15	1	I	-----	8331. 12	2	------	I	-----
8139. 10	30	2	I	-----	8333. 19	2h	------	I	-----
8140. 90	2	------	I	-----	8335. 27	2	------	I	-----
8143. 62	60	7	I	-----	8338. 07	60	8	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
A					*A*				
8339.35	2	------	I	-----	8558.22	1	------	I	-----
8340.42	2	------	I	-----	8560.59	1	------	I	-----
8342.44	3	------	I	-----	8561.04	1	------	I	-----
8344.25	400	80	I	3	8563.66	3	------	I	-----
8346.36	2	------	I	-----	8563.83	2	------	I	-----
8352.55	5	------	I	-----	8564.10	1	------	I	-----
8357.68	1	4	II	-----	8569.04	80	15	I	-----
8358.56	1	2	II?	-----	8572.34	1	------	I	-----
8359.13	2	------	I	-----	8575.06	1	2	II?	-----
8361.29	20	4	I	-----	8581.89	10	30	II	-----
8367.91	1	------	I	-----	8586.54	8	1	I	-----
8375.38	1	------	I	-----	8587.84	1	------	I	-----
8376.00	1	------	I	-----	8589.89	1	------	I	-----
8380.05	80	8	I	-----	8592.06	20	2	I	-----
8382.98	100	10	I	-----	8597.83	5	------	I	-----
8384.52	1	3?	II	-----	8599.87	10	1	I	-----
8385.03	40	5	I	-----	8603.32	60	8	I	-----
8391.63	10	2	I	-----	8609.98	50	6	I	-----
8394.99	20	2	I	-----	8610.86	7	1	I	-----
8399.12	3	------	I	-----	8614.81	1	------	I	-----
8399.98	40	3	I	-----	8624.83	20	2	I	-----
8402.58	2	------	I	-----	8628.28	1	------	I	-----
8403.23	1	------	I	-----	8636.36	10	1?	I	-----
8404.57	3	------	I	-----	8640.04	2500	500	I	3
8404.89	20	2	I	-----	8644.31	20	2	I	-----
8407.84	1	------	I	-----	8653.35	2	------	I	-----
8408.11	5	------	I	-----	8655.40	5	------	I	-----
8416.26	2	------	I	-----	8656.12	7	1	I	-----
8425.76	10	2	I	-----	8657.60	1	------	I	-----
8427.38	3	------	I	-----	8658.23	20	2	I	-----
8434.98	1	------	I	-----	8659.03	6	------	I	-----
8435.65	1	------	I	-----	8660.92	3	10	II	-----
8439.31	8	1	I	-----	8661.68	40	4	I	-----
8440.51	1	------	I	-----	8671.37	10	1	I	-----
8441.42	20	2	I	-----	8673.87	30	3	I	-----
8442.14	1	------	I	-----	8683.60	2	------	I	-----
8447.31	1	------	I	-----	8689.58	1	------	I	-----
8451.69	50	5	I	-----	8690.37	2	------	I	-----
8453.26	6	1	I	-----	8699.27	1	2	II	-----
8454.00	60	7	I	-----	8709.17	5	------	I	-----
8460.00	500	120	I	2	8711.20	600	100	I	2
8465.36	2	------	I	-----	8715.58	70	10	I	-----
8471.46	3	------	I	-----	8716.70	10	------	I	-----
8475.37	40	3	I	-----	8725.09	1	2h	II	-----
8477.51	1	------	I	-----	8728.66	1	------	I	-----
8478.06	1	------	I	-----	8737.03	4	------	I	-----
8487.10	2	------	I	-----	8749.15	40	4	I	-----
8493.16	3	------	I	-----	8749.41	20	2	I	-----
8506.53	5	------	I	-----	8763.88	10	1	I	-----
8508.15	50	5	I	-----	8764.71	1	------	I	-----
8513.55	1	------	I	-----	8765.17	6	------	I	-----
8513.69	2	------	I	-----	8765.43	1	------	I	-----
8514.18	4	------	I	-----	8767.04	1	------	I	-----
8514.82	8	1	I	-----	8795.54	4	------	I	-----
8516.03	1	------	I	-----	8804.34	------	2	II	-----
8521.37	1	------	I	-----	8815.11	3	------	I	-----
8527.70	1	------	I	-----	8821.12	1	------	I	-----
8527.91	3	------	I	-----	8823.95	1	------	II	-----
8532.47	1	------	I	-----	8825.24	20	2	I	-----
8546.43	2500	500	I	7	8828.79	1	------	I	-----

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity: Tube	Intensity: Spark	Spectrum	Zeeman type	Wavelength in air	Intensity: Tube	Intensity: Spark	Spectrum	Zeeman type
A					*A*				
8841. 99	20	2	I		9482. 83	10	1	I	
8845. 95	5		I		9483. 52	1		I	
8871. 65	1		I		9493. 42	1		I	
8875. 92	10		I		9498. 81	30	3	I	
8876. 17	5		I		9506. 10	2		I	
8886. 72	3		I		9513. 14	600	100	I	
8888. 43	1		I		9514. 37	8	3	I	
8902. 06	4		I		9524. 87	1		I	
8906. 81	1		I		9553. 63	1		I	
8918. 06	2		I		9563. 26	200	50	I	
8927. 24	3		I		9566. 01	1		I	
8952. 14	5		I		9581. 37	10	3	I	
8958. 89	20		I		9587. 35	5		I	
8967. 15	10		I		9613. 15	3		I	
8976. 65	20		I		9616. 05	5	2	I	
8994. 77	30	2	I		9628. 91	1		I	
9004. 74	200	20	I		9652. 05	50	7	I	
9031. 77	2		I		9654. 41	3		I	
9035. 66	1		I		9662. 40	1		I	
9052. 35	10	3	I		9673. 88	10	2	I	
9093. 88	2		I		9697. 66	15	3	I	
9138. 20	30	3	I		9716. 80	3		I	
9145. 58	3		I		9722, 30	4	1	I	
9153. 00	2		I		9737. 93	4	1	I	
9158. 55	9		I		9746. 45	2		I	
9177. 23	100	8	I		9752. 40	20	10	I	
9179. 30	4		I		9754. 43	1		I	
9182. 14	250	40	I		9791. 20	1		I	
9193. 30	300	30	I		9793. 40	1		I	
9216. 86	10		I		9801. 09	10	4	I	
9243. 18	1		I		9805. 71	2		I	
9250. 25	1000	150	I		9828. 22	15	4	I	
9282. 54	4		I		9864. 37	1		I	
9295. 63	15	1	I		9877. 96	1		I	
9299. 95	60	5	I		10023. 30	2		I	
9306. 16	2		I		10036. 53	150	40	I	
9306. 79	1		I		10088. 51	40	8	I	
9308. 29	9		I		10103. 88	15	3	I	
9313. 65	2		I		10112. 20	10	2	I	
9314. 46	2		I		10120. 15	3		I	
9325. 14	80	10	I		10135. 30	6	3	I	
9341. 17	3		I		10168. 81	20	4	I	
9342. 00	2		I		10181. 45	2		I	
9346. 32	150	20	I		10184. 18	1		I	
9359. 86	1		I		10190. 70	2		I	
9365. 75	3		I		10203. 90	2		I	
9372. 00	1		I		10207. 78	8	1	I	
9380. 14	50	7	I		10208. 74	2		I	
9387. 54	3		I		10209. 56	1		I	
9387. 94	2		I		10227. 18	20	6	I	
9389. 91	1		I		10259. 15	30	6	I	
9402. 57	50	4	I		10259. 67	10		I	
9404. 14	4	2	I	II	10293. 33	1		I	
9405. 18	1		I		10312. 19	1		I	
9412. 23	2		I		10319. 65	2		I	
9453. 75	12	2	I		10342. 55	3		I	
9488. 25	12	2	I		10361. 40	2		I	
9469. 05	1		I		10377. 83	2		I	
9472. 01	1		I		10388. 31	8		I	
9474. 26	1		I		10389. 01	1		I	

TABLE 1. *Emission spectra of hafnium*—Continued

Wavelength in air	Intensity		Spectrum	Zeeman type	Wavelength in air	Intensity		Spectrum	Zeeman type
	Tube	Spark				Tube	Spark		
10397. 45	200	50	I		10859. 40	1		I	
10405. 51	5		I		10868. 44	20	2	I	
10414. 09	3		I		10876. 28	1		I	
10418. 99	6	1	I		10882. 85	1		I	
10423. 78	400	150	I		10900. 75	15	5	I	
10438. 63	2		I		10914. 47	50	10	I	
10445. 17	7		I		10923. 38	2		I	
10457. 92	1		I		10933. 82	10		I	
10472. 68	1		I		10938. 08	2		I	
10479. 20	1		I		10953. 12	4		I	
10480. 21	200	30	I		10971. 61	50	5	I	
10484. 44	3		I		11000. 00	3		I	
10496. 77	3		I		11030. 13	20	1	I	
10499. 16	1		I		11039. 01	4		I	
10517. 74	1		I		11046. 97	40	4	I	
10527. 28	25	3	I		11074. 42	5		I	
10529. 38	2		I		11092. 58	1		I	
10545. 50	7	1	I		11139. 05	20		I	
10547. 44	1		I		11190. 17	1		I	
10550. 85	100	7	I		11219. 28	1		I	
10588. 44	1		I		11227. 70	10		I	
10594. 89	50	5	I		11229. 01	15	1	I	
10622. 14	12	1	I		11242. 16	3		I	
10634. 81	5		I		11296. 74	1		I	
10637. 93	150	30	I		11303. 44	10		I	
10642. 30	1		I		11365. 02	25	7	I	
10661. 35	2		I		11393. 12	1		I	
10698. 21	1		I		11480. 61	15	2	I	
10755. 89	1		I		11602. 16	4		I	
10756. 97	1		I		11766. 95	10		I	
10762. 68	3		I		11960. 80	2		I	
10772. 33	15	2	I		12043. 08	6		I	
10784. 36	10	3	I						
10815. 24	2		I						
10851. 65	6	1	I						

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Dielectric Constant of Hydrogen-Bonded Liquids

Floyd Buckley

A simple extension is presented of Onsager's electrostatic theory of dielectric polarization to take account of the "excess" polarization due to hydrogen bonding. Dielectric data for a number of liquid mixtures are analyzed and the deviations from ideal behavior expressed in terms of an excess polarization. A method is developed for calculating the excess polarization and certain related molecular parameters. Tentative values of these parameters have been determined for some particularly simple structures.

1. Introduction

The influence of molecular shape on the dielectric constant of polar liquids has been considered in an earlier paper [1].[1] The phenomenological theory of Onsager was shown to give a generally satisfactory description of the dielectric constant (1) of pure liquids as a function of the temperature, and (2) of a large class of binary mixtures as a function of the composition. For the restricted class of compounds studied it was found unnecessary to assume specific interactions between nearest neighbors.

The purpose of the present paper is to describe a simple extension of the electrostatic theory to the class of polar liquids that can be considered to possess a pseudo-lattice structure. The order shown by this class is assumed to reflect the existence of strong, specific interactions between neighboring systems. The results of the calculations for a series of related mixtures suggest that the incorporation of these elements of order and interaction into the phenomenological representation of Onsager suffices to give a reasonable agreement with experimental data. A more rigorous analysis along the lines suggested could lead to useful information on the energies of molecular interaction in liquids.

2. Pure Liquids

The class of liquids consisting of water and the lower members of the series of normal aliphatic alcohols is considered first to determine the order of magnitude of the polarizability of the hydrogen bonds characteristic of these substances.

2.1. Model

The Onsager model of a polar liquid represents a molecule by a cavity with a polarizable point-dipole placed at the center. The volume, shape, polarizability, and intrinsic moment of the cavity are assumed to be the same as those of the molecule. The calculation of the dielectric polarization neglects short-range forces of interaction between neighbors, and assumes that the influence of long-range forces is fully accounted for by the reaction field produced by the polarization of the continuous dielectric medium surrounding the cavity.

[1] Figures in brackets indicate the literature references at the end of this paper.

In the equivalent representation of a polar liquid which exhibits structure, the molecular cavity of the preceding model is replaced by a representative cluster of molecules that defines a "cell" or "cage" with properties determined, in part, by the local structure. Whereas the intrinsic moment of a cell is taken as characteristic of the molecule within the cell, the "effective" volume, shape, and polarizability of the cell are assumed to depend on the number and polarizability of the bonds (contacts) with nearest neighbors. Each bond is characterized by an interaction energy (strength) and a polarizability that is shared by the cells in contact. In the following discussion it is assumed that the strengths of the bonds are sufficiently weak to permit the dipole to orient freely within its cell. All cooperative effects arising from dipolar interactions are therefore neglected. Actually, it is necessary to assume only that the lifetime of a given molecular cluster is short in comparison with its characteristic relaxation time.

This approach to the problem of the static dielectric constant of hydrogen-bonded liquids is in marked contrast to that of the Kirkwood theory. In the latter, primary attention is focused on the determination of correlation factors and equilibrium constants that characterize the interaction of neighboring dipoles. In the present treatment, attention is centered on the calculation of the polarization of a representative cell (cluster, cavity, molecule) as a function of cell shape, bond polarizabilities, and bond-interaction energies. In view of the quite different information that results from the electrostatic treatment, it was thought worthwhile to investigate this approach as a useful alternative to that of Kirkwood.

2.2. Polarization

The calculation of the dielectric polarization follows the procedure of Onsager. The selection of the parameters characteristic of a cell is not unique and at present can be defended only on the grounds of reasonableness. In the present calculations, the intrinsic moment and shape of a cavity are assumed to be "equal" to those of the free molecule, and the remaining parameters, volume and polarizability, are fixed by the conditions:

(a) $\lim_{\lambda \to 0} \mathscr{P} = \mathscr{P}_e$(electronic + atomic + bonding)

(b) $\lim_{\lambda \to \infty} \mathscr{P} = \mathscr{P}_e + \mathscr{P}_0$(orientation).

The molar dielectric polarization, $\mathscr{P}$, is given by

$$\mathscr{P}=(\epsilon-1)V=\left\{\frac{R_e}{1-(R_e/V_c)gk_R}+\frac{4\pi N}{9kT}\frac{\mu^2k_c}{(1-(R_e/V_c)gk_R)^2}\right\}\frac{9\epsilon}{2\epsilon+1},$$

in which V_c/N is the volume of a cell, g, k_R, and k_c are the reaction field and cavity parameters [1], R_e is the effective molar refraction, and all other symbols have their usual significance.

The only parameter which is assumed to depend on the temperature is the effective refraction, R_e. This means that if the average contribution of each bond (contact) to the polarizability of the cell is independent of the temperature, then $R_e-(R_D+P_A)=R_e-A$ is proportional to the average number of bonds or "degree of association" of a cell as a function of the temperature. From another point of view, the variation in R_e-A is a measure of the fluctuation in the density of polarizability at the boundary of the cell.

The volume of the characteristic cell of a pure liquid should be calculable from a general theory of the liquid state. Although it is not possible at present to do this, any reasonable choice of volume will suffice, because in the simple electrostatic theory the variation of R_e with the temperature is probably more significant than the absolute values of R_e. The principal condition on V_c/N is that it must be large enough to enclose the polarizability of the bonds to nearest neighbors.

2.3. Representation of Experimental Data

Characteristic cell data are given in table 1 and auxiliary data in table 2. In table 1, V_c is the molar cavity volume and, except for water, is taken as the molar volume at the melting point. The quantity r_c is the radius of a spherical cavity corresponding to V_c/N; μ, and ϵ are, respectively, the values of the dipole moment and eccentricity assigned to the cavity; and r_{12}^{mp} is the contribution to the polarizability of a cell of each bond between neighboring cells. In table 2, R_D is the molar refraction for the Na–D line; P_A is the contribution of atomic polarization to the total distortion polarization A; R_e^{mp} is the value of the effective distortion polarization R_e at the melting point; and $\epsilon_{\lambda=0}$ (diel) and $\epsilon_{\lambda=0}$ (disp) are, respectively, the high frequency dielectric constants determined by the conditions given above and from dielectric dispersion data.

The procedure adopted in selecting the values of the cell parameters was the following: It was first assumed that maximum coordination existed at the melting point. The coordination numbers for H—O . . . H bonds were then taken as 4 for water and 3 for each of the alcohols. It was further assumed that the polarizabilities of all H—O . . . H bonds were the same with a value chosen to match the theory to the data for water. The values of dipole moment and eccentricity given in table 1 for water were assigned to the Onsager cavity and the cavity

TABLE 1. *Characteristic cell data*

Substance	V_c	r_c	μ_D	ϵ_{oblate}	r^{mp}_{12}
	cm^3	A			cm^3 bond^{-1} mole^{-1}
HOH	40.3	2.52	1.85	0.80	2.3
CH_3OH	34.2	2.39	1.70	.60	2.3
C_2H_5OH	51.0	2.72	1.70	.70	2.3
n-C_3H_7OH	68.0	3.00	1.70	.80	2.3
n-C_4H_9OH	85.0	3.23	[a](1.67)	.85	2.3
i-C_3H_7OH	68.0	3.00	1.70	.80	2.3
t-C_4H_9OH	95.0	3.35	1.70	.50	2.3

[a] Quantities in parentheses are estimated.

TABLE 2. *Auxiliary data*

Substance	mp	R_D	R_e^{mp}	[a]$A=R_D+P_A$	$\epsilon^{20°}_{\lambda=0}$ (diel)	$\epsilon^{20°}_{\lambda=0}$ (disp)
	°C	cm^3	cm^3	cm^3		
HOH	0	3.67	13.1	4.0	5.3_2	5.2
CH_3OH	−97.8	8.2	15.5	8.7	3.1_3	5.9
C_2H_5OH	−117.3	12.8	22.5	15.6	2.9_2	3.8
n-C_3H_7OH	−127.	17.7	27.1	20.2	2.7_7	2.7
n-C_4H_9OH	−89.8	22.1	32.1	25.2	2.6_3	3.2
i-C_3H_7OH	−89.5	17.5	27.1	20.2	2.6_1	[b](3.2)
t-C_4H_9OH	25.5	[b](22.1)	34.5	[b](27.6)	2.6_1[25°]	[b](2.8)[25°]

[a] Estimates from dielectric data on gases.
[b] Quantities in parentheses are estimated.

volume and effective distortion polarization were determined to fit the dielectric data at the melting point. These data were $\epsilon_{\lambda=\infty}=88.0$ and $\epsilon_{\lambda=0}=5.5$. The cell parameters are sensitive to the choice of values for $\epsilon_{\lambda=\infty}$ and $\epsilon_{\lambda=0}$, but any reasonable selection near the values adopted will suffice for an exploratory study.

For the alcohols, the molar cavity volume V_c was estimated as the molar volume at the melting point, the dipole moments given in table 1 were assigned, the values of $R_e^{mp}=A+3\times2.23$ [2] were calculated, and the eccentricities were then determined to fit the dielectric data. This choice of cavity volume was made because of the relatively large uncertainty in the values of $\epsilon_{\lambda=0}$. There is the additional restriction that this volume must be at least equal to the molar volume.

2.4. Water

The available data for liquid water extend from the freezing temperature to the critical temperature and cover a range in density of approximately 1 to 0.5 g/cm^3 [2,3]. Recent data on superheated steam at temperatures slightly above the critical temperature extend over a range in density of 0.50 to 0.10 g/cm^3 [4].

The variation of the dielectric polarization with temperature (or density) is completely accounted for by the variation in the effective molar refraction of a representative cell shown in figures 1 and 2. This dependence of R_e on the temperature (or density) can also be translated into a dependence of the "degree of association" on the temperature if the

[2] Values used in the computations deviated slightly from the rounded number 2.3.

fraction associated is defined by:

$$f=\frac{R_e-A}{R_e^{mp}-A}.$$

The dependence of f on the temperature is graphically represented in figure 4. An alternative view is that the average coordination number remains constant and the change in R_e reflects a corresponding change in the interaction energies and bond polarizabilities between nearest neighbors. This view is adopted in the treatment of mixtures.

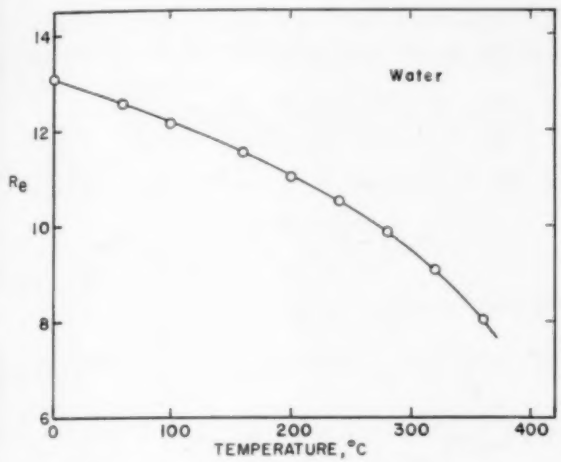

FIGURE 1. *Variation of the effective molar refraction of water from the melting point to the critical temperature.*

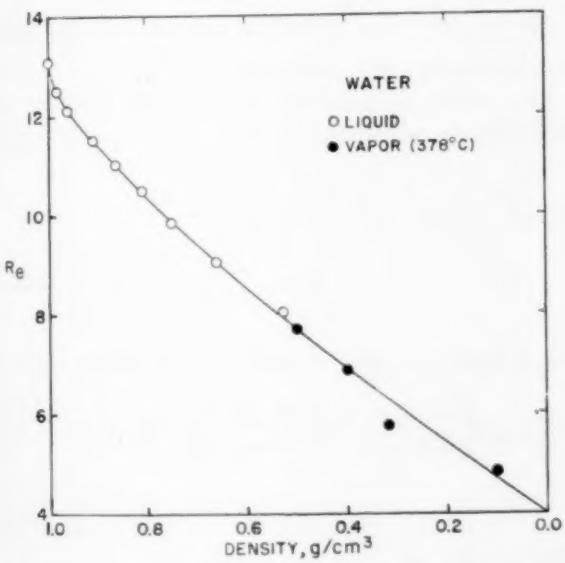

FIGURE 2. *Dependence of the effective molar refraction of water on density.*

2.5. Alcohols

Data over a wide temperature range are available for only a few of the simpler aliphatic alcohols. Cell characteristics and associated data are given in tables 1 and 2, and the polarizabilities adjusted to fit the polarization data are represented in figure 3. The fraction associated as a function of the temperature is shown in figure 4.

The strong similarity in dielectric behavior within this class of compounds (including water) is striking, if not entirely unexpected. The anomalous behavior of *t*-butylalcohol, if real, is noteworthy.

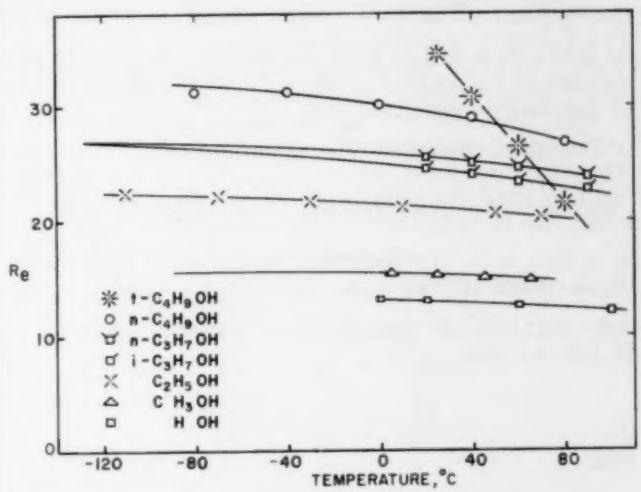

FIGURE 3. *Dependence of the effective molar refraction on temperature.*

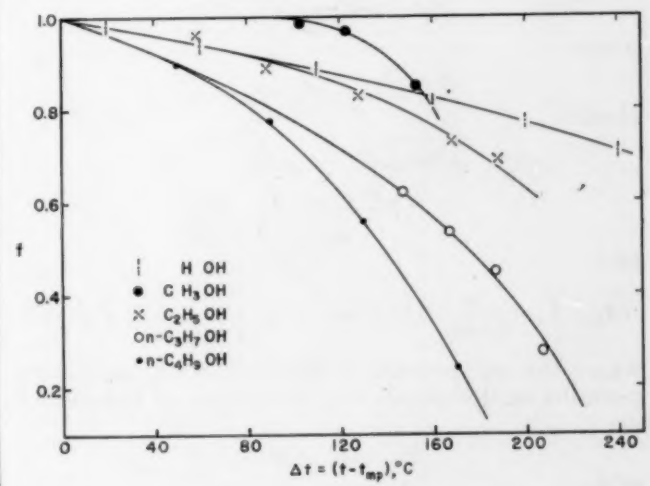

FIGURE 4. *Dependence of the degree of association on the temperature interval above the melting point.*

3. Mixtures

3.1. Preliminary Remarks

The objective is to express the dielectric polarization of an Onsager spheroidal cavity containing a polarizable point-dipole in terms of an associated orientational partition function.

According to electrostatic theory, the field acting on the dipole is

$$\vec{E}=\vec{E}_c+\vec{E}_R \qquad \vec{E}_R=g\cdot\vec{M},$$

where $\vec{E}_c$ is the field produced within the cavity by external sources, and $\vec{E}_R$ is the reaction field arising from the polarization of the medium outside the cavity. The total moment of the cavity is $\vec{M}$ and g is a factor that depends on the shape and volume of the cavity, and on the dielectric constant of the surrounding medium.

The total moment $\vec{M}$ can be written

$$\vec{M}=\vec{\mu}+\alpha\vec{E}_{c\|}+\alpha g_{\|}\vec{M}_{\|}+\alpha\vec{E}_{c\perp}+\alpha g_{\perp}\vec{M}_{\perp}=\vec{M}_{\|}+\vec{M}_{\perp},$$

in which α is the isotropic polarizability, $\vec{\mu}$ is the dipole moment, and the subscripts $\|$ and $\perp$ designate components parallel and perpendicular to $\vec{\mu}$. It follows that

$$\vec{M}_{\|}=\frac{\vec{\mu}}{1-\alpha g_{\|}}+\frac{\alpha\vec{E}_c}{1-\alpha g_{\|}}$$

and

$$\vec{M}_{\perp}=\frac{\alpha\vec{E}_{c\perp}}{1-\alpha g_{\perp}}.$$

The total energy of the cavity is

$$\mathscr{E}=-\vec{\mu}\cdot\vec{E}-\frac{1}{2}\vec{M}_{\mu=0}\cdot\vec{E}_c,$$

where

$$\vec{E}=\vec{E}_c+g_{\|}\vec{M}_{\|}+g_{\perp}\vec{M}_{\perp}.$$

Hence

$$\vec{\mu}\cdot\vec{E}=\vec{\mu}\cdot\vec{E}_c+g_{\|}\vec{\mu}\cdot\vec{M}_{\|}$$

$$=\frac{\mu E_1\mathscr{L}\cos\theta}{1-\alpha g_{\|}}+\frac{\mu^2 g_{\|}}{1-\alpha g_{\|}}$$

and

$$\vec{M}_{\mu=0}\cdot\vec{E}_c=\frac{\alpha}{1-\alpha g_{\|}}(E_1\mathscr{L}\cos\theta)^2+\frac{\alpha}{1-\alpha g_{\perp}}(E_1\mathscr{M}\sin\theta)^2,$$

where the components of the field inside the cavity, parrallel and perpendicular to the axis of the cavity, are

$$E_{c\|}=E_1\mathscr{L}\cos\theta,$$

and

$$E_{c\perp}=E_1\mathscr{M}\sin\theta,$$

and the external field $\vec{E}_1$ makes an angle θ with the axis of the spheroid containing the dipole. The depolarization factors $\mathscr{L}$ and $\mathscr{M}$ are known.

The self-energy of the cavity is

$$\mathscr{E}_s=\mathscr{E}_{E_1=0},$$

so that the total energy of the cavity produced by the external field is

$$\mathscr{E}_c=\mathscr{E}-\mathscr{E}_s=\frac{-\mu E_1}{1-\alpha g_{\|}}\mathscr{L}\cos\theta-\frac{1}{2}\frac{\alpha}{1-\alpha g_{\|}}$$

$$(E_1\mathscr{L}\cos\theta)^2-\frac{1}{2}\frac{\alpha}{1-\alpha g_{\perp}}(E_1\mathscr{M}\sin\theta)^2.$$

The component of the moment of the cavity along $\vec{E}_1$ is

$$M_{E_1}=M_{\|}\cos\theta+M_{\perp}\sin\theta$$

$$=\frac{\mu\cos\theta}{1-\alpha g_{\|}}+\frac{\alpha E_1\mathscr{L}\cos^2\theta}{1-\alpha g_{\|}}+\frac{\alpha E_1\mathscr{M}\sin^2\theta}{1-\alpha g_{\perp}},$$

and can be written

$$M_{E_1}=-\left(\frac{\partial}{\partial E_1\mathscr{L}}+\frac{\partial}{\partial E_1\mathscr{M}}\right)\mathscr{E}_c.$$

Hence the average component is

$$\overline{M}_{E_1}=\int_0^{\pi}\frac{1}{2}M_{E_1}e^{-\mathscr{E}_c/kT}\sin\theta d\theta\Big/\int_0^{\pi}\frac{1}{2}e^{-\mathscr{E}_s/kT}\sin\theta d\theta$$

$$=kT\left(\frac{\partial}{\partial E_1\mathscr{L}}+\frac{\partial}{\partial E_1\mathscr{M}}\right)lnQ_c,$$

where

$$Q_c=\int_0^{\pi}\frac{1}{2}e^{-\mathscr{E}_c/kT}\sin\theta d\theta$$

is the orientational partition function of the cavity associated with the external field $\vec{E}_1$.

The partition function Q_c can be written to a sufficient approximation as

$$Q_c\cong e^{\frac{1}{2}\alpha\left\{\frac{(E_1\mathscr{L}\cos\theta)^2}{1-\alpha g_{\|}}+\frac{(E_1\mathscr{M}\sin\theta)^2}{1-\alpha g_{\perp}}\right\}^{\text{ave.}}\Big/kT}$$

$$\int_{\frac{1}{2}}^{e}e^{\frac{\mu E_1\mathscr{L}\cos\theta}{1-\alpha g_{\|}}\Big/kT}\sin\theta d\theta,$$

and if the usual approximations are made

$$lnQ_c=\frac{1}{2}\alpha\left\{\frac{1}{3}\frac{(E_1\mathscr{L})^2}{1-\alpha g_{\|}}+\frac{2}{3}\frac{(E_1\mathscr{M})^2}{1-\alpha g_{\perp}}\right\}\Big/kT+$$

$$\frac{1}{6}\frac{\mu^2(E_1\mathscr{L})^2}{(1-\alpha g_{\|})^2}\frac{1}{(kT)^2}$$

Hence

$$M_{E1}=\left[\alpha\left(\frac{1}{3}\frac{\mathscr{L}}{1-\alpha g_{\|}}+\frac{2}{3}\frac{\mathscr{M}}{1-\alpha g_{\perp}}+\frac{1}{3}\frac{\mu^2\mathscr{L}}{kT(1-\alpha g_{\|})^2}\right)\right]E_1,$$

which is in agreement with former results [1].

The dielectric constant is related to $\overline{M}_{E_1}$ by the fundamental relation

$$\epsilon-1=4\pi\frac{N}{V}\frac{\overline{M}_{E_1}}{E_1},$$

so that the molar polarization becomes [1]

$$\mathscr{P}=(\epsilon-1)V=4\pi N\left\{\left(\frac{1}{3}\frac{\alpha\mathscr{L}}{1-\alpha g_{\|}}+\frac{2}{3}\frac{\alpha\mathscr{M}}{1-\alpha g_{\perp}}\right)+\frac{1}{3kT}\frac{\mu^2\mathscr{L}}{(1-\alpha g_{\|})^2}\right\}.$$

The relation of the polarization of an Onsager cell to the orientational partition function Q_c is utilized in the following section.

3.2. Binary Mixtures

The polarization of an ideal mixture is

$$\mathscr{P}_{12}=\mathscr{P}_1x_1+\mathscr{P}_2x_2,$$

and for a real mixture

$$\mathscr{P}_{12}=\mathscr{P}_1x_1+\mathscr{P}_2x_2+\Delta\mathscr{P}_m$$

in which $\mathscr{P}_1$ and $\mathscr{P}_2$ for the pure components take account of the long-range forces of interaction (Onsager) and the polarization of mixing $\Delta\mathscr{P}_m$ allows for the specific interactions of nearest neighbors. An approximate calculation of $\Delta\mathscr{P}_m$ can be made in the following way.

Let

$z_1=z_2=z$=average number of nearest neighbors to cells (or clusters) of species 1 and 2, respectively,

n_{11}=number of cells of species 1 having only symmetrical 1-1 bonds,

n_{22}=number of cells of species 2 having only symmetrical 2-2 bonds,

n_{1j}=number of cells of species 1 having j unsymmetrical bonds of type 1-2,

n_{2j}=number of cells of species 2 having j unsymmetrical bonds of type 2-1.

Cells of species 1 have a molecule of type 1 at the center of the cell, and those of species 2 have a molecule of type 2 at the center of the cell. Let w_{11}, w_{22}, w_{1j}, and w_{2j} denote the energies of the respective types of cells. Then the total configurational energy of N_1 cells of type 1 and N_2 cells of type 2 can, to a first approximation, be taken as the sum of an energy of "chemical" binding

$$\mathscr{E}_b=n_{11}w_{11}^{(b)}+n_{22}w_{22}^{(b)}+\Sigma n_{1j}w_{1j}^{(b)}+\Sigma n_{2j}w_{2j}^{(b)}$$

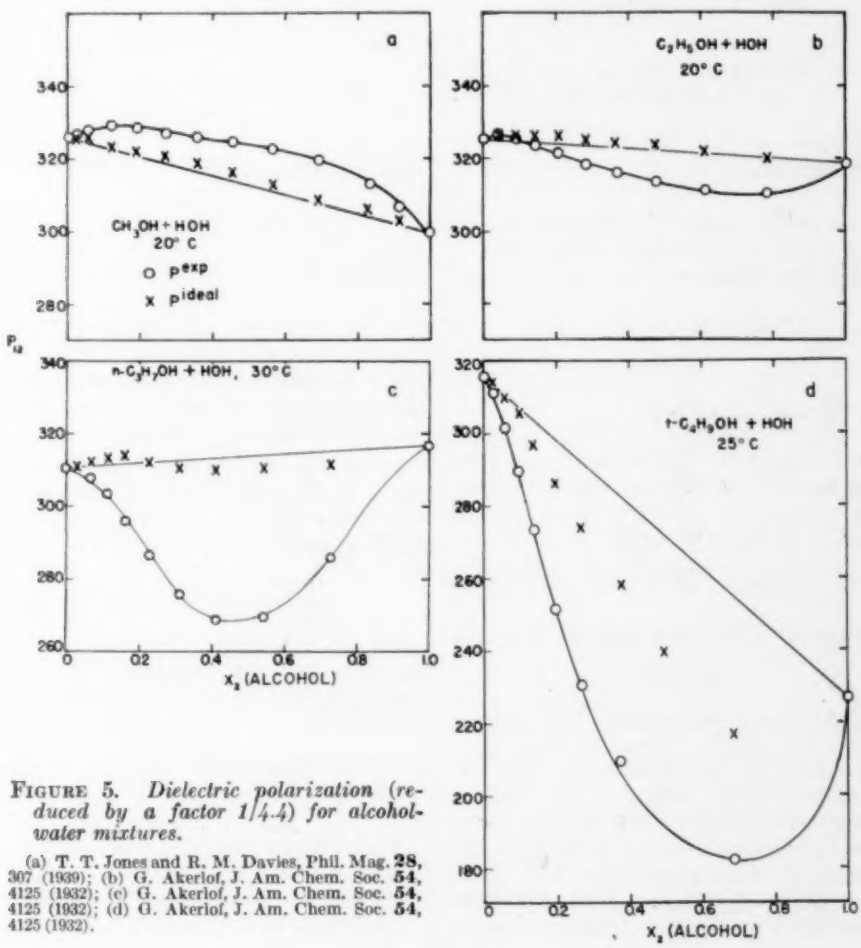

FIGURE 5. *Dielectric polarization (reduced by a factor 1/4.4) for alcohol-water mixtures.*

(a) T. T. Jones and R. M. Davies, Phil. Mag. **28**, 307 (1939); (b) G. Akerlof, J. Am. Chem. Soc. **54**, 4125 (1932); (c) G. Akerlof, J. Am. Chem. Soc. **54**, 4125 (1932); (d) G. Akerlof, J. Am. Chem. Soc. **54**, 4125 (1932).

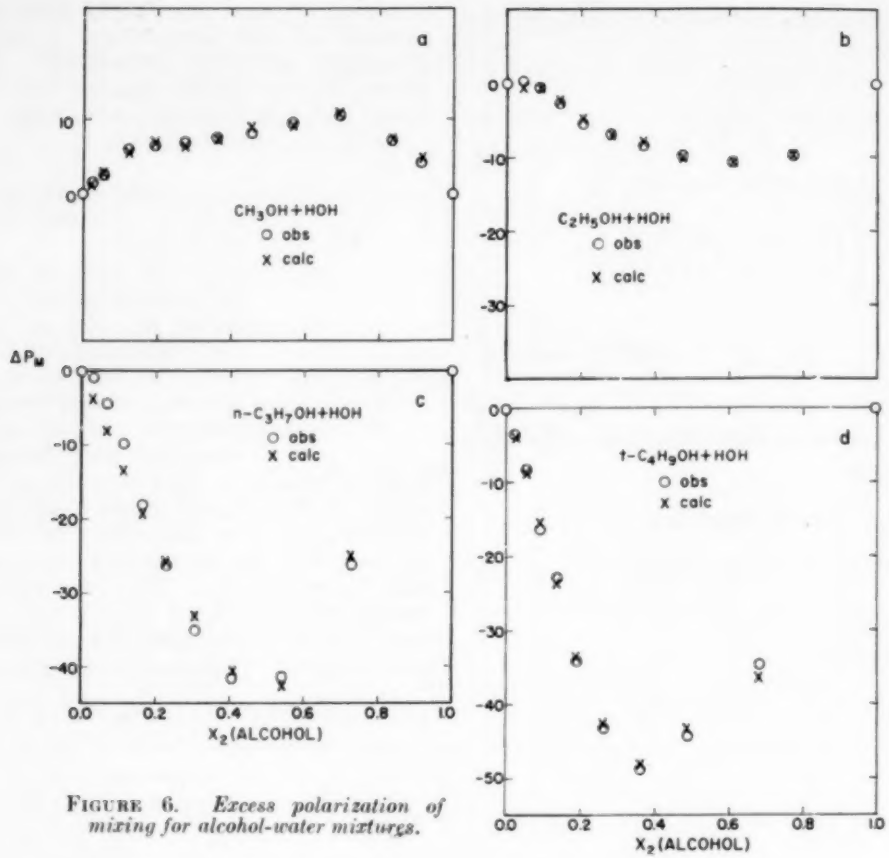

FIGURE 6. *Excess polarization of mixing for alcohol-water mixtures.*

and an energy of polarization

$$\mathscr{E}_P = n_{11}w_{11}^{(P)} + n_{22}w_{22}^{(P)} + \Sigma n_{1j}w_{1j}^{(P)} + \Sigma n_{2j}w_{2j}^{(P)}.$$

The N's must satisfy the relations

$$n_{11} + \Sigma n_{1j} = N_1,$$

and

$$n_{22} + \Sigma n_{2j} = N_2.$$

These relations can be used to eliminate n_{11} and n_{22} from the expression for $\mathscr{E}_P$ to give

$$\mathscr{E}_P = N_1 w_{11}^{(P)} + N_2 w_{22}^{(P)} + \sum n_{1j}(w_{1j}^{(P)} - w_{11}^{(P)}) + \sum n_{2j}(w_{2j}^{(P)} - w_{22}^{(P)}) = \mathscr{E}_P^0 + \Delta\mathscr{E}_P.$$

The partition function for the system can be written

$$Q = \Sigma\Sigma Q_1 \cdot Q_2 \cdot g(N_1, N_2, n_{12}^*, n_{21}^*) e^{-\Delta\mathscr{E}_P/kT},$$

in which Q_1 and Q_2 are the partition functions for the species 1 and 2, respectively, and contain factors which include all contributions to the energy other that $\Delta\mathscr{E}_P$. The configurational factor g denotes the number of equivalent configurations for fixed N_1, N_2, $n_{12}^* = \Sigma n_{1j}$, and $n_{21}^* = \Sigma n_{2j}$. The partition function ΔQ_m associated with the polarization of mixing is therefore

$$\Delta Q_m = \Sigma g(N_1, N_2, n_{12}^*, n_{21}^*) \cdot e^{-\Delta\mathscr{E}_P/kT},$$

and to the zeroth approximation can be replaced by

$$\Delta Q_m^{(0)} = g(N_1, N_2, \overline{n}_{12}^*, \overline{n}_{21}^*) e^{-\overline{\Delta\mathscr{E}_P}/kT},$$

in which all variables in ΔQ_m have been replaced by average or equilibrium values (denoted by a bar).

The energies of polarization of the Onsager cells appearing in $\overline{\Delta\mathscr{E}_P}$ have the same functional form as that evaluated for the Onsager cavity in the case of the pure liquid. Hence the average values $\overline{w}_{12}^{(P)}$ and $\overline{w}_{21}^{(P)}$ appearing in

$$\overline{\Delta\mathscr{E}_P} = \overline{n}_{12}^*(\overline{w}_{12}^{(P)} - \overline{w}_{11}^{(P)}) + \overline{n}_{21}^*(\overline{w}_{21}^{(P)} - \overline{w}_{22}^{(P)})$$

can be calculated by the method described under section 3.1, "Preliminary Remarks". The "excess polarization" associated with the mixing process is therefore

$$\Delta P_m = \frac{\overline{n}_{12}^*}{N}(\overline{\mathscr{P}}_{12} - \overline{\mathscr{P}}_1) + \frac{\overline{n}_{21}^*}{N}(\overline{\mathscr{P}}_{21} - \overline{\mathscr{P}}_2),$$

in which $\overline{\mathscr{P}}_{12}$ and $\overline{\mathscr{P}}_{21}$, depend on the composition not only through the reaction field, but also through the "effective polarizability" contributed to a cell by the bonds to its nearest neighbors.

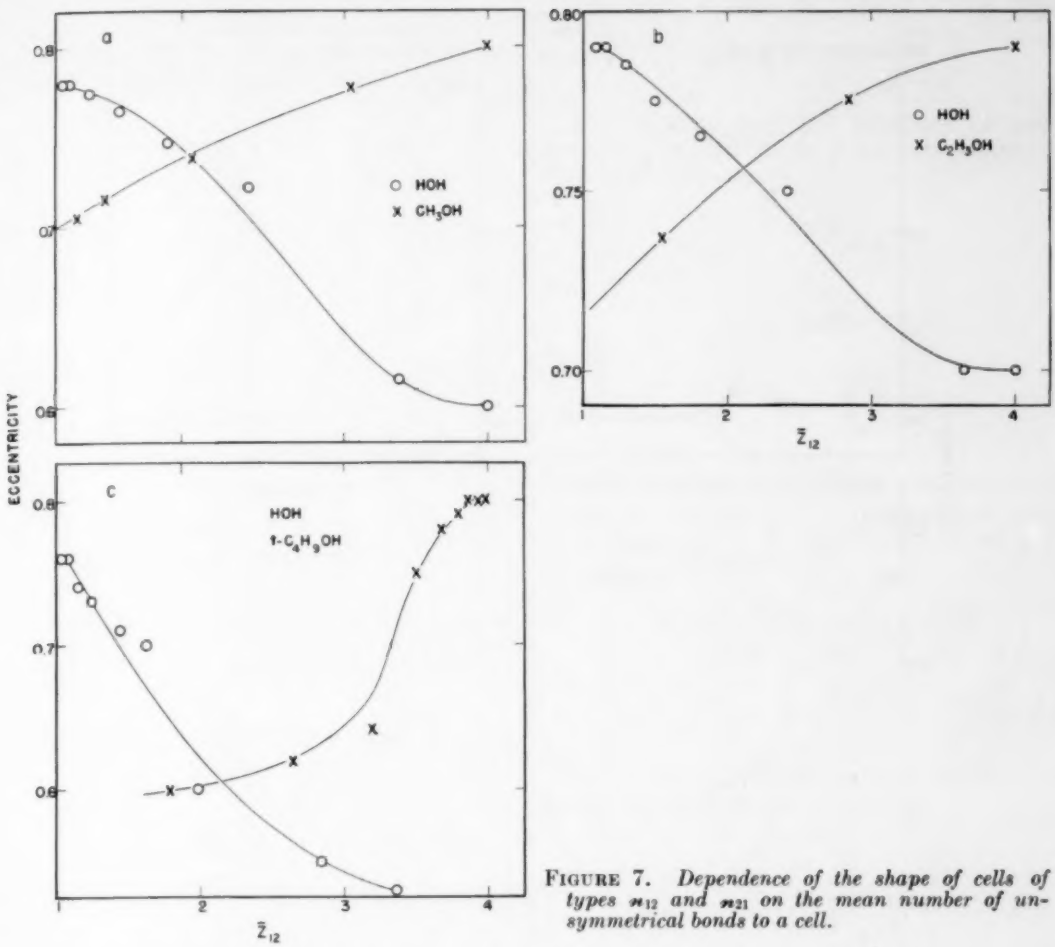

FIGURE 7. *Dependence of the shape of cells of types n_{12} and n_{21} on the mean number of unsymmetrical bonds to a cell.*

Estimates of $\overline{n_{12}^*}$ and $\overline{n_{21}^*}$ can be made by using the method introduced by Bethe. The general model of the mixture is that consisting of $\mathcal{N}_1$ and $\mathcal{N}_2$ molecules of species 1 and 2, respectively, distributed over a lattice of $\mathcal{N}=\mathcal{N}_1+\mathcal{N}_2$ sites, in such a way that each site has $z=z_1=z_2$ nearest neighbors. This shell of nearest neighbors about a central molecule defines the general boundary of an Onsager cell. Its volume, shape, polarizability, and moment need not be specified. The method adopted for determining $\overline{n_{12}^*}$ and $\overline{n_{21}^*}$ is taken from the work of Rushbrooke [5].

The statistical weight of all configurations with a molecule of species 1 at the center of the complex is

$$Q_1=\lambda_1 v_1\{x_{11}\lambda_1 v_1+\epsilon x_{12}\lambda_2 v_2\}^z=\lambda_1 v_1[Q_1]^z,$$

in which λ_1 is the absolute activity, v_1 the local partition function, and the x_{1j} are bond-interaction factors of the form $e^{-2w_1^b/zkT}$. The quantity ϵ is an "occupational factor" which allows for the interaction of a peripheral molecule of a cell with the surrounding environment. A similar expression is assigned to molecules of species 2:

$$Q_2=\lambda_2 v_2\{\epsilon x_{21}\lambda_1 v_1+x_{22}\lambda_2 v_2\}^z=\lambda_2 v_2[Q_2]^z.$$

The statistical weight of the entire assembly is $Q=Q_1+Q_2$.

The equilibrium numbers of molecules of the two species are

$$\mathcal{N}_1=\frac{\mathcal{N}}{z+1}\cdot\lambda_1\cdot\frac{\partial}{\partial\lambda_1}\ln Q_1$$

and

$$\mathcal{N}_2=\frac{\mathcal{N}}{z+1}\cdot\lambda_2\cdot\frac{\partial}{\partial\lambda_2}\ln Q_2,$$

and the numbers of unsymmetrical bonds $z\overline{\mathscr{P}}$ associated with either of the two types of cells are

$$\overline{\mathscr{P}}=\frac{1}{2}\frac{\mathcal{N}}{z}\cdot x_{12}\frac{\partial}{\partial x_{12}}\ln Q$$

$$=\frac{1}{2}\frac{\mathcal{N}}{z}\cdot x_{21}\frac{\partial}{\partial x_{21}}\ln Q.$$

The condition that a central and peripheral site are equivalent can be expressed by the relation

$$\lambda_1\frac{\partial Q_1}{\partial\lambda_1}=\lambda_2\frac{\partial Q_2}{\partial\lambda_2},$$

which leads to

$$\epsilon=\frac{[Q_1]^{z-1}}{[Q_2]^{z-1}}.$$

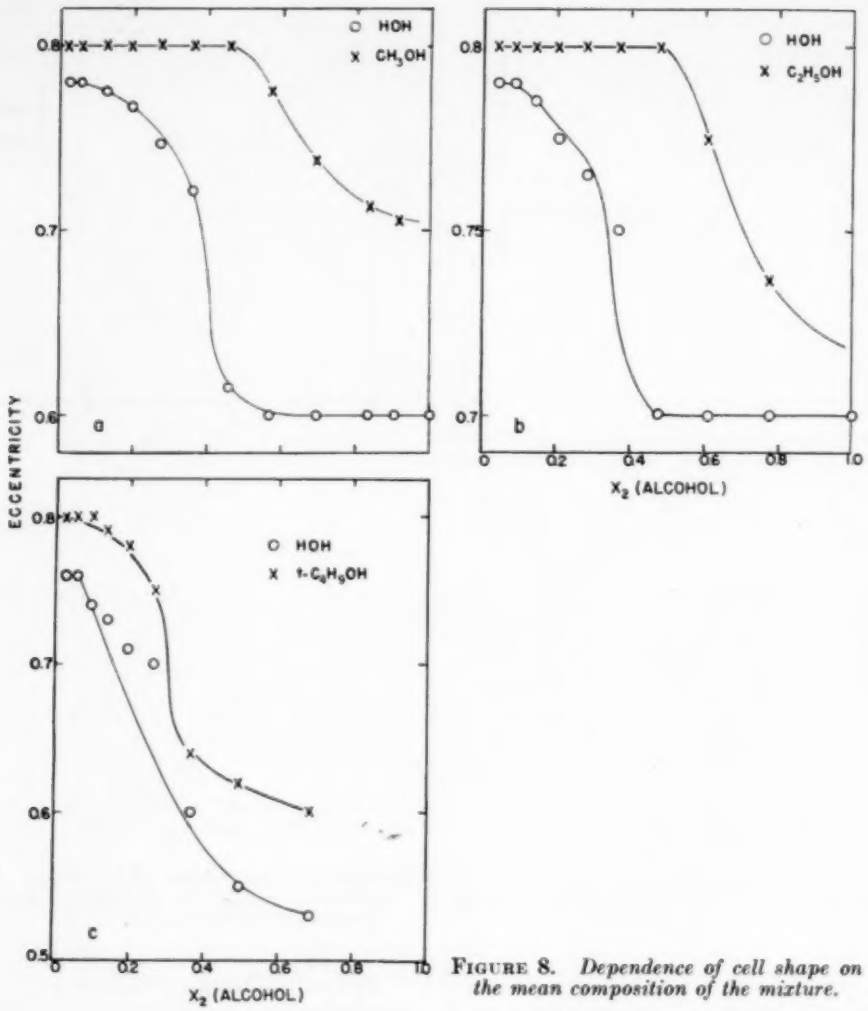

FIGURE 8. *Dependence of cell shape on the mean composition of the mixture.*

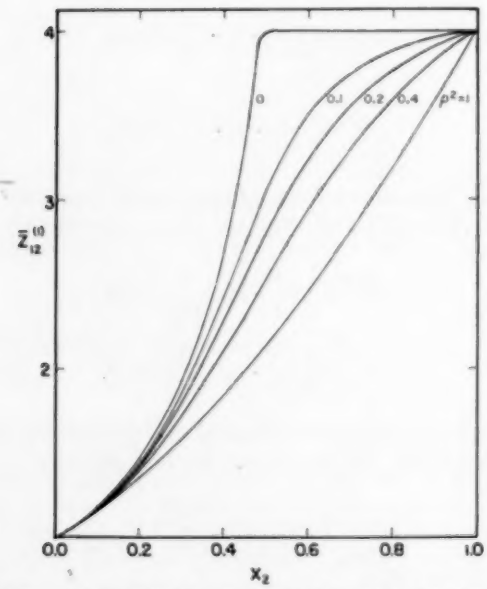

FIGURE 9. *A family of curves representing the dependence of the mean number of unsymmetrical bonds on the mean composition of the mixture and the cell interaction parameter ρ.*

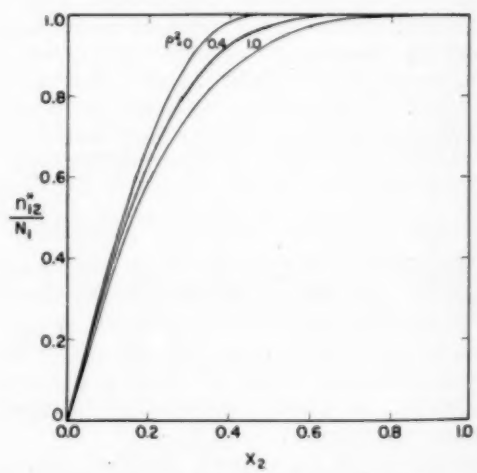

FIGURE 10. *A family of curves representing the dependence of the fraction of unsymmetrical cells of species 1 on the mean composition of the mixture and the cell interaction parameter ρ.*

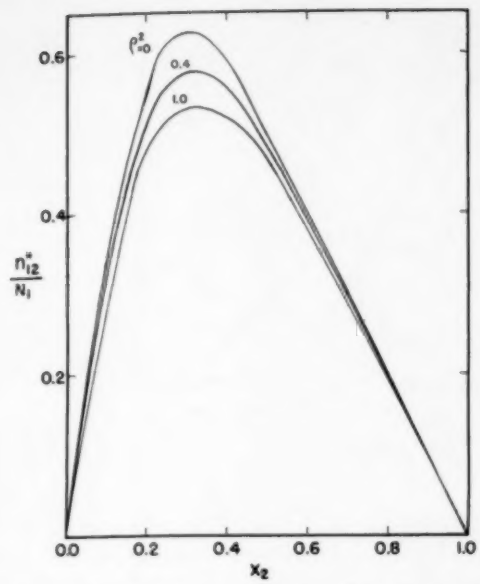

FIGURE 11. *A family of curves representing the dependence of the fraction of all cells of species 1 that have unsymmetrical bonds on the mean composition of the mixture and the interaction parameter ρ.*

With the aid of this relation it follows that

$$\mathcal{N}_1=\mathcal{N}\cdot Q_1/Q$$

and

$$\mathcal{N}_2=\mathcal{N}\cdot Q_2/Q,$$

and $\overline{\mathcal{Y}}$ satisfies the equation of a quasi-chemical equilibrium:

$$(\mathcal{N}_1-\overline{\mathcal{Y}})(\mathcal{N}_1-\overline{\mathcal{Y}})=\overline{\mathcal{Y}}^2\,\frac{x_{11}x_{22}}{x_{12}^2},$$

where $x_{12}=x_{21}$. The solution of this equation is

$$\overline{\mathcal{Y}}=\mathcal{N}\cdot x_1x_2\cdot\frac{1}{1+\gamma},$$

$$\gamma=\sqrt{1+4x_1x_2(\rho^2-1)}$$

and

$$\rho^2=\frac{x_{11}x_{22}}{x_{12}^2},$$

in which x_1 and x_2 are the mole fractions of the two species in the assembly.

The statistical weight of all cells of species 1 which have only symmetrical 1-1 bonds is $\lambda_1v_1(x_{11}\lambda_1v_1)^z$ and the corresponding weight of all cells of species 1 with unsymmetrical 1-2 bonds is $Q_1-\lambda_1v_1(x_{11}\lambda_1v_1)^z$. Hence the numbers of the two classes of cells satisfy the relations

$$\frac{\overline{n}_{12}^*}{\overline{n}_{11}}=\frac{[Q_1]^z}{(x_{11}\lambda_1v_1)^z}-1$$

and

$$\overline{n}_{12}^*+\overline{n}_{11}=\mathcal{N}_1,$$

from which it follows that

$$\overline{n}_{12}^*=\left\{1-\left[1-\frac{\overline{\mathcal{Y}}}{\mathcal{N}_1}\right]^z\right\}\mathcal{N}_1.$$

In a similar way the numbers of cells, $\overline{n}_{12}^{(j)}$, of species 1 which have j unsymmetrical 1-2 bonds satisfy the equations

$$\frac{\overline{n}_{12}^{(j)}}{\overline{n}_{11}}=f_1^{(j)}$$

and

$$\Sigma\overline{n}_{12}^{(j)}=\overline{n}_{12}^*,$$

so that

$$\overline{n}_{12}^{(j)}=\frac{f_1^{(j)}}{\Sigma f_1^{(j)}}\cdot\overline{n}_{12}^*.$$

The $f_1^{(j)}$ are the terms of degree j in the polynomial that expresses the ratio of the statistical weight of all cells of species 1 to the weight of all cells of type $\overline{n}_{11}$. This polynomial is:

$$\left(\frac{x_{11}\lambda_1v_1+\epsilon x_{12}\lambda_2v_2}{x_{11}\lambda_1v_1}\right)^z=\left(1+\frac{\overline{\mathcal{Y}}}{\mathcal{N}_1-\overline{\mathcal{Y}}}\right)^z$$
$$=\left(1+\frac{x_2\cdot 2/1+\gamma}{1-x_2\cdot 2/1+\gamma}\right)^z.$$

The fraction of cells of species 1 for the configuration with j unsymmetrical bonds is

$$\frac{\overline{n}_{12}^{(j)}}{\overline{n}_{12}}=\frac{\left(\frac{x_2\cdot 2/1+\gamma}{1-x_2\cdot 2/1+\gamma}\right)^j}{\left(1+\frac{x_2\cdot 2/1+\gamma}{1-x_2\cdot 2/1+\gamma}\right)^z-1}=F_1^{(j)}.$$

Similar expressions hold for cells of species 2. Thus:

$$\overline{n}_{21}^*=\left\{1-\left[1-\frac{\overline{\mathcal{Y}}}{\mathcal{N}_2}\right]^z\right\}\mathcal{N}_2,$$

and

$$\frac{\overline{n}_{21}^{(j)}}{\overline{n}_{21}^*}=\frac{\left(\frac{x_1\cdot 2/1+\gamma}{1-x_1\cdot 2/1+\gamma}\right)^j}{\left(1+\frac{x_1\cdot 2/1+\gamma}{1-x_1\cdot 2/1+\gamma}\right)^z-1}=F_2^{(j)}.$$

The required expression for the excess polarization now becomes

$$\Delta\mathcal{P}_m=\Sigma\frac{\overline{n}_{12}^{(j)}}{\mathcal{N}}(\overline{\mathcal{P}}_{12}^{(j)}-\overline{\mathcal{P}}_1)+\Sigma\frac{\overline{n}_{21}^{(j)}}{\mathcal{N}}(\overline{\mathcal{P}}_{21}^{(j)}-\overline{\mathcal{P}}_2)$$
$$=\frac{\overline{n}_{12}^*}{\mathcal{N}}\Sigma F_1^{(j)}(\overline{\mathcal{P}}_{12}^{(j)}-\overline{\mathcal{P}}_1)+\frac{\overline{n}_{12}^*}{\mathcal{N}}\Sigma F_2^{(j)}(\overline{\mathcal{P}}_{21}^{(j)}-\overline{\mathcal{P}}_2),$$

in which the $\overline{\mathcal{P}}_{12}^{(j)}$ and $\overline{\mathcal{P}}_{21}^{(j)}$ are the polarizations of the Onsager cells corresponding to the j-configurations for cells of species 1 and 2, respectively. In the subsequent analysis of experimental data, the

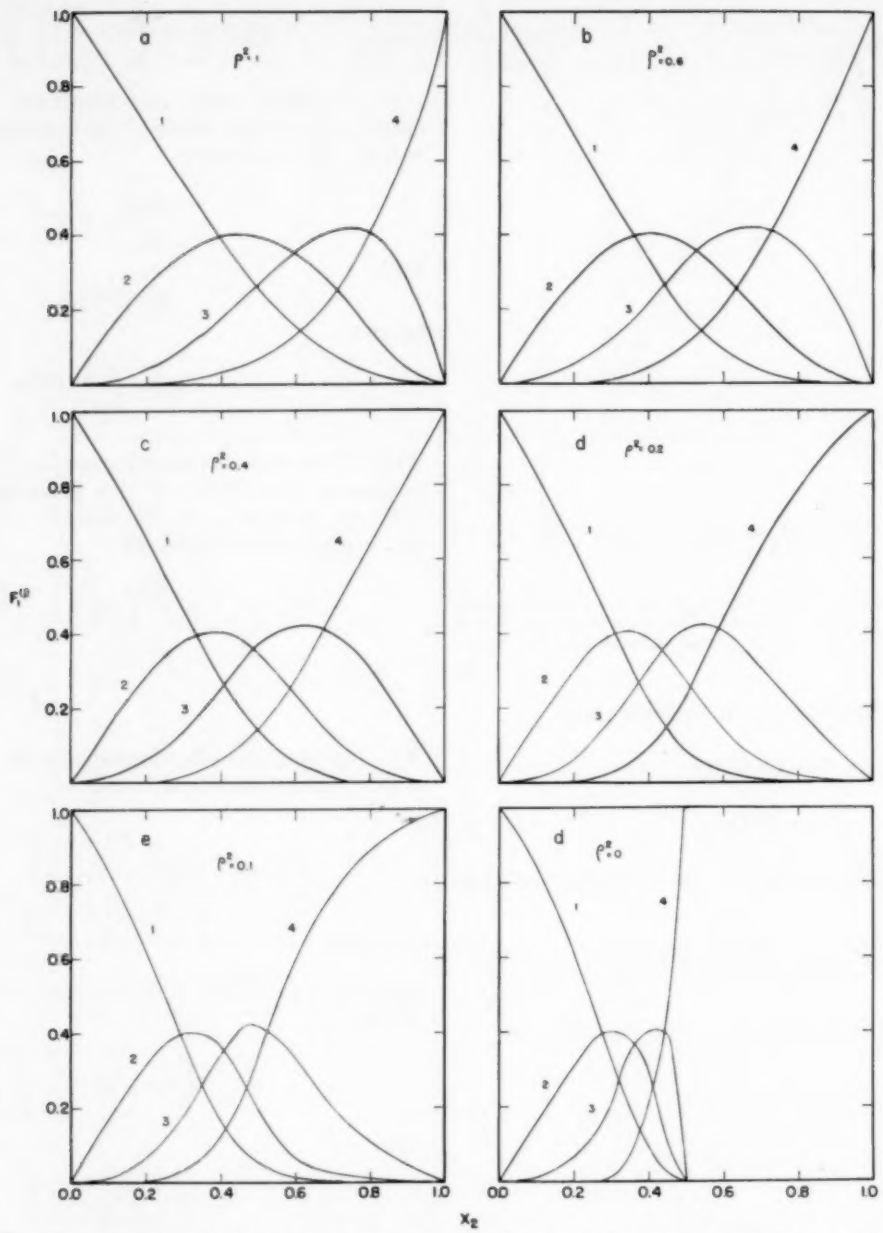

FIGURE 12. *A family of curves representing the dependence on composition and interaction parameter ρ of the fractions of cells of species 1 that have 1, 2, 3, 4 unsymmetrical bonds.*

quantities $\Sigma F_1^{(j)}\overline{\mathscr{P}_{12}^{(j)}}$ and $\Sigma F_2^{(j)}\overline{\mathscr{P}_{21}^{(j)}}$ are replaced by $\overline{\mathscr{P}_{12}^{(j)}}$ and $\overline{\mathscr{P}_{21}^{(j)}}$, which are the polarizations of the corresponding Onsager cells with average configurations: $\bar{z}_{12}=\Sigma j\cdot F_1^{(j)}$ and $\bar{z}_{21}=\Sigma j\cdot F_2^{(j)}$.

4. Representation of Experimental Data

In the preceding discussion it has been assumed that all unsymmetrical bonds binding a cell of either species to its environment are equivalent. This means that $x_{12}=x_{21}$. This assumption obviously expresses only a very crude approximation of the interactions in a cluster. Nevertheless, it is doubtful that the obvious refinement of dividing the bonds to any cell into classes $\alpha, \beta, \ldots$ with approximately equal interaction factors $x_{12}^{(\alpha)}=x_{21}^{(\alpha)}$; $x_{12}^{(\beta)}=x_{21}^{(\beta)}, \ldots$ compensates for the added complexity. The simpler picture is retained in the subsequent discussion of special cases.

The analysis of experimental data is reduced to a calculation of the excess polarization of mixing, $\Delta\mathscr{P}_m$. In the absence of knowledge of the specific properties of the clusters occurring in a given mixture, such as volume, shape, bond energies, and bond polarizabilities, the calculation becomes one of adjusting the values of selected parameters. This adjustment can be done in a number of ways, but the general procedure adopted was first to choose characteristic bond polarizabilities $r_{12}^{(j)}=r_{21}^{(j)}$ and aver-

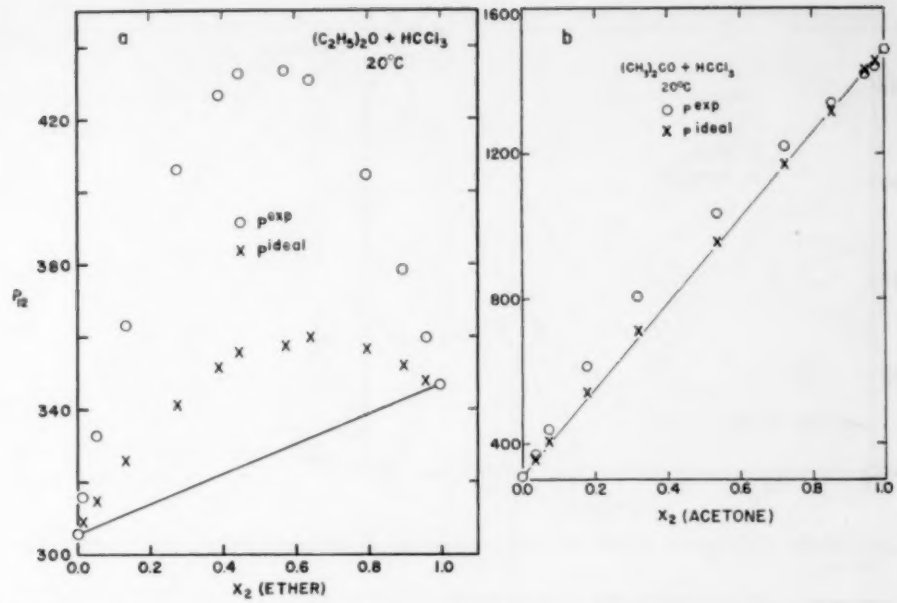

FIGURE 13. *Dielectric polarizations of chloroform-ether and chloroform-acetone mixtures.*
(a) D. P. Earp and S. Glasstone, J. Chem. Soc. **1935,** 1709; (b) D. P. Earp and S. Glasstone, J. Chem. Soc. **1935,** 1709.

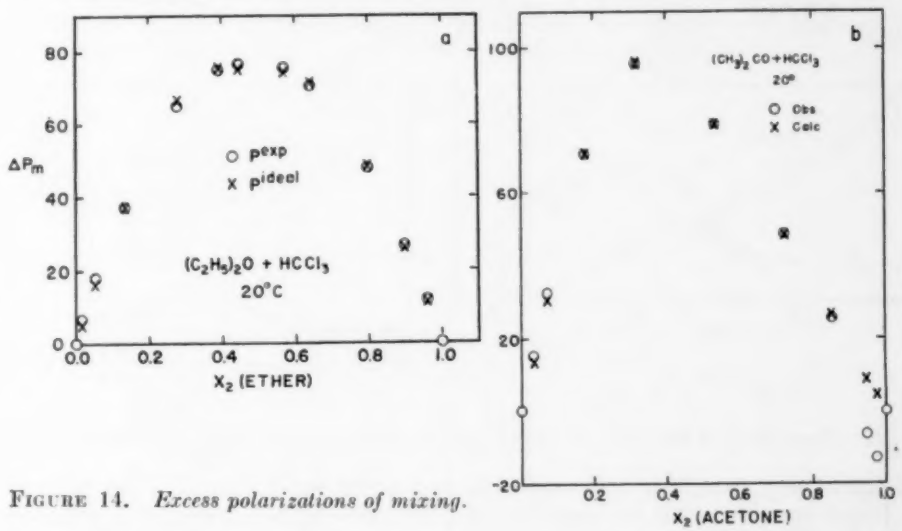

FIGURE 14. *Excess polarizations of mixing.*

age bond interaction factors $\overline{x_{12}^{(j)}} = \overline{x_{21}^{(j)}}$ and then, if an additional adjustment was necessary, to allow the shapes of the cells to vary with the composition of the boundary of the cell.

For the simplest case all unsymmetrical bonds are equivalent and the eccentricities of cells of types $\overline{\pi}_{1j}$ and $\overline{\pi}_{2j}$ are those of the pure species. The determination of $\overline{r}_{12}$ is most easily made from the deviations observed at great dilution. At one end of the concentration scale $\overline{z}_{12}=1$ and $\overline{z}_{21}=z$; at the other end $\overline{z}_{12}=z$ and $\overline{z}_{21}=1$. At either end the value of $\Delta\mathscr{P}_m$ is very insensitive to the values of the interaction factors x_{11}, x_{22}, and x_{12}, and these factors can be eliminated by setting them equal to unity (equivalent to setting the bond-interaction energies equal to zero). Moreover, the contribution to $\Delta\mathscr{P}_m$ from cells of the component present in small amount becomes negligible at high dilution. Hence, in principle, one calculation suffices to determine $\overline{r}_{12}$. The value of the interaction function $\rho^2 = x_{11}x_{22}/x_{12}^2$ is now fixed by the value of $\Delta\mathscr{P}_m$ at any arbitrary concentration, though preferably at the concentration for which $\Delta\mathscr{P}_m$ is near a maximum.

In more complex cases, the eccentricities of the cells in the mixtures are functions of composition. Although in these cases the direct calculation of the eccentricities of the various kinds of cells, and of the characteristic mean interaction parameter is, in principle, possible, it is doubtful if the data warrant such a detailed calculation. The values given for these characteristics for any mixture were determined by trial. The method of adjusting these values was as follows: Estimates of the mean eccentricity of cells of type $\overline{\pi}_{1j}$ (or $\overline{\pi}_{2j}$) were made on the assumption

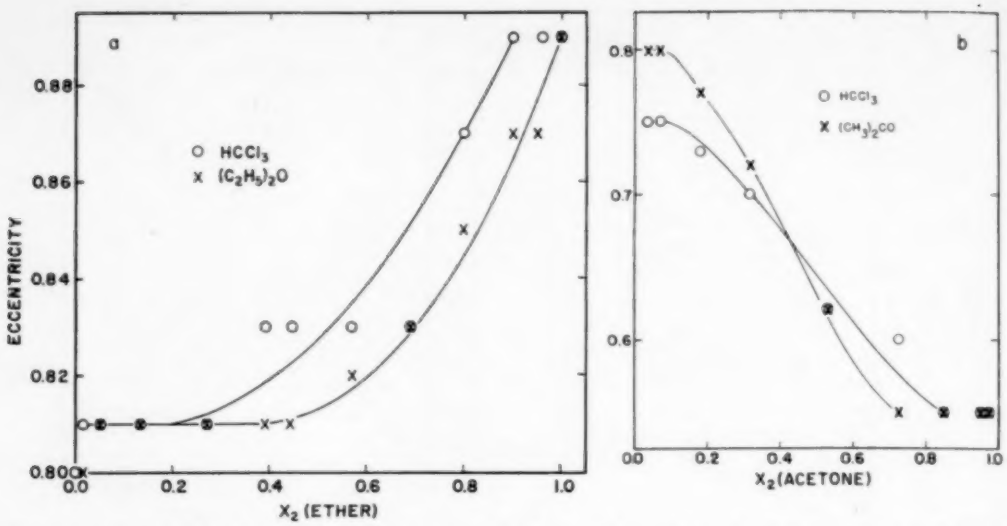

FIGURE 15. *Dependence of the shape of cells of types n_{12} and n_{21} on the mean number of unsymmetrical bonds to a cell.*

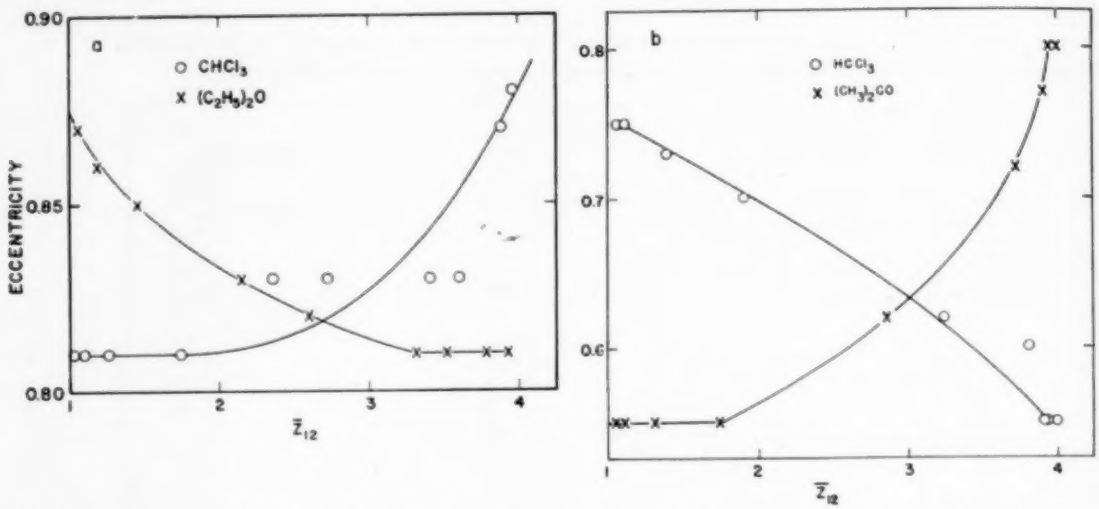

FIGURE 16. *Dependence of the shape of cells of types n_{12} and n_{21} on the mean composition of the mixture.*

that the eccentricity of any species of cell varied in approximately a linear manner with the number of unsymmetrical bonds. Values were then calculated for a composition near that corresponding to a maximum $\Delta\mathscr{P}_m$, and the value of ρ was adjusted to give the observed value of $\Delta\mathscr{P}_m$. The mean eccentricities for other concentrations were determined by trial.

In the more general case there are several classes of bonds, each class distinguished by an interaction factor such as $x_{12}^{(a)}$. This distinction of classes is neglected in the calculation of (1) the average number of cells of a given kind, and (2) the average number of unsymmetrical bonds to that cell; but some distinction of classes is recognized in the calculation of the polarizability characteristic of a given cell. In fact each class of bonds is assigned (a) a characteristic bond polarizability, and (b) a position on a scale of relative bond-strengths. The latter permits the determination of the structure of the periphery of a cell for a given $\bar{z}_{12}$ (or $\bar{z}_{21}$), and in conjunction with the former, allows the calculation of the effective polarizability of the cell.

4.1. Mixtures of Water and Alcohols

The calculations of mean eccentricities for cells of type $\bar{n}_{1j}$ and $\bar{n}_{2j}$ were made under the following simplifying assumptions; (a) $z=4$ (one C–H . . . O and three O–H . . . O bonds), (b) $x_{12}=x_{21}$, and (c) $\rho^2 << 1$ (except for *t*-Bu OH). The choice of $z=4$ for the alcohols differs from the value, $z=3$, chosen for the pure liquids and implies that for the purpose of calculating the relative numbers of cells of various types, the interaction parameters for all bonds to the alcohol cells are equal, that is $x_{\text{O–H}\,\ldots\,\text{O}}=x_{\text{C–H}\,\ldots\,\text{O}}$. This assumption cannot be true, but in view of the crudeness of the model and the gain in simplicity of treatment for the symmetrical case, its adoption is justified for the calculation of effective

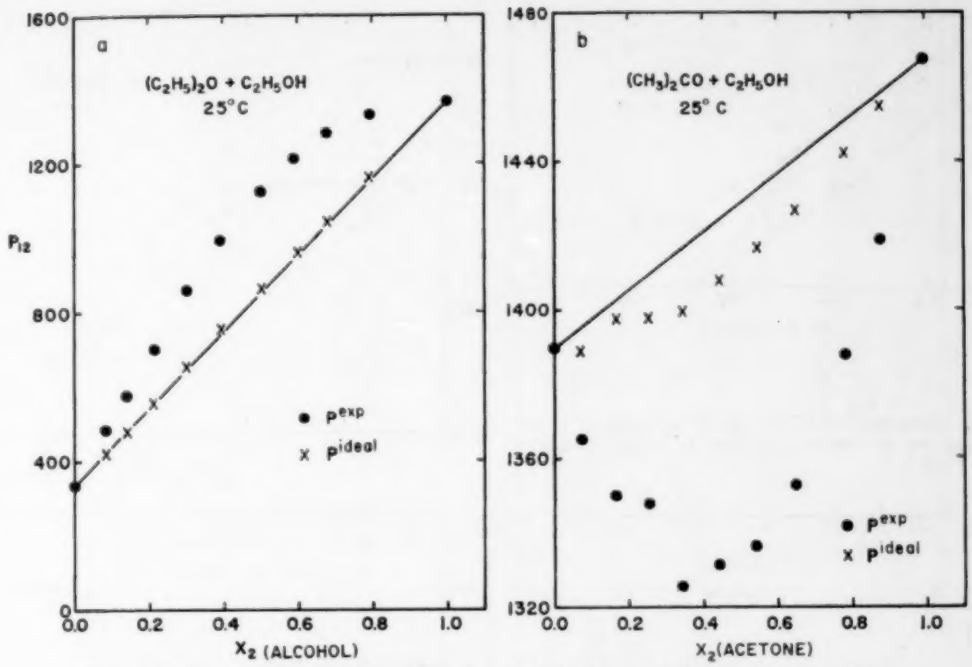

FIGURE 17. *Dielectric polarizations for alcohol-ether and alcohol-acetone mixtures.*
(a) J. Wyman, Jr., J. Am. Chem. Soc. **55**, 4116 (1933); (b) W. Graffunder and E. Heyman, Z. Physik. **72**, 744 (1931).

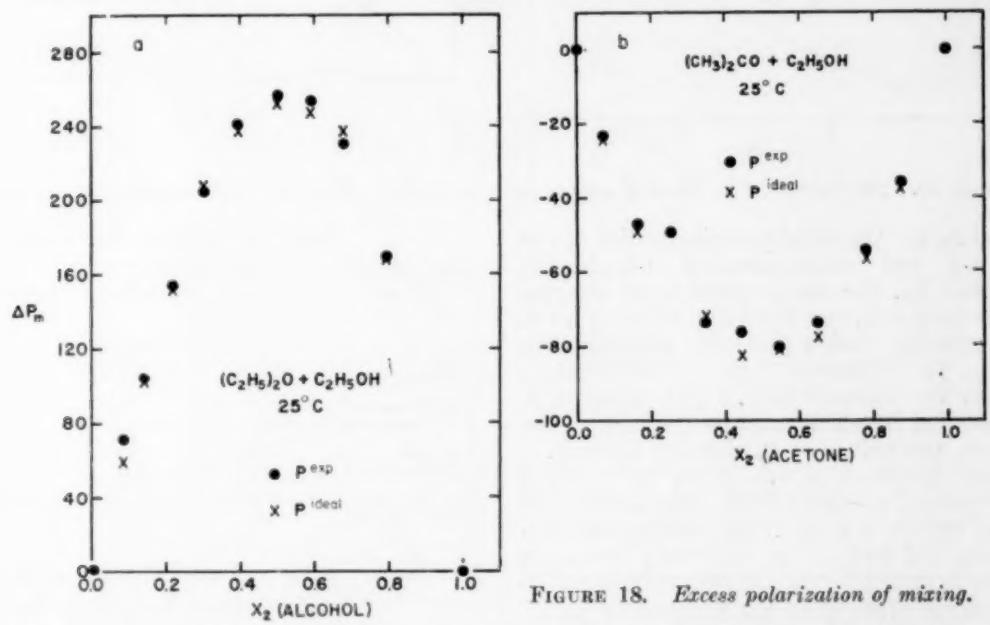

FIGURE 18. *Excess polarization of mixing.*

mean shapes. Assumption (c) implies that

$$-\overline{N}\overline{w}_{cell}=N(-2\overline{w}_{12}+\overline{w}_{11}+\overline{w}_{22})>>2RT.$$

The calculated eccentricities are relatively insensitive to values of ρ for which $\rho^2<<1$ so that for these cases $-N\overline{w}_{cell}>8RT$(4.8 K cal at 25° C).

In the calculation of the "effective polarizability" of the average cell of either species, two additional assumptions are made: (d) bonds of type C–H . . . O do not contribute to the polarizability, and (e) the interaction parameters $x_{O-H...O}$ and $x_{C-H...O}$ are "sufficiently" different so that O—H . . . O bonds are saturated before C—H . . . O bonds are formed. Assumptions (b) and (e) are actually contradictory, but in view of the simplification effected they can be taken as compatible for the two types of calculation. Under these restrictions the polarizability of a water cell (species 1) is

$$\begin{aligned}R_e^{cell}&=R_D^{(1)}+\{\overline{z}_{12}r_{12}+(z-\overline{z}_{12})r_1\}\\&=R_e^{(1)}-\overline{z}_{12}(r_1-r_{12})\\&=R_e^{(1)}-\overline{z}_{12}\cdot\delta r_{12},\end{aligned}$$

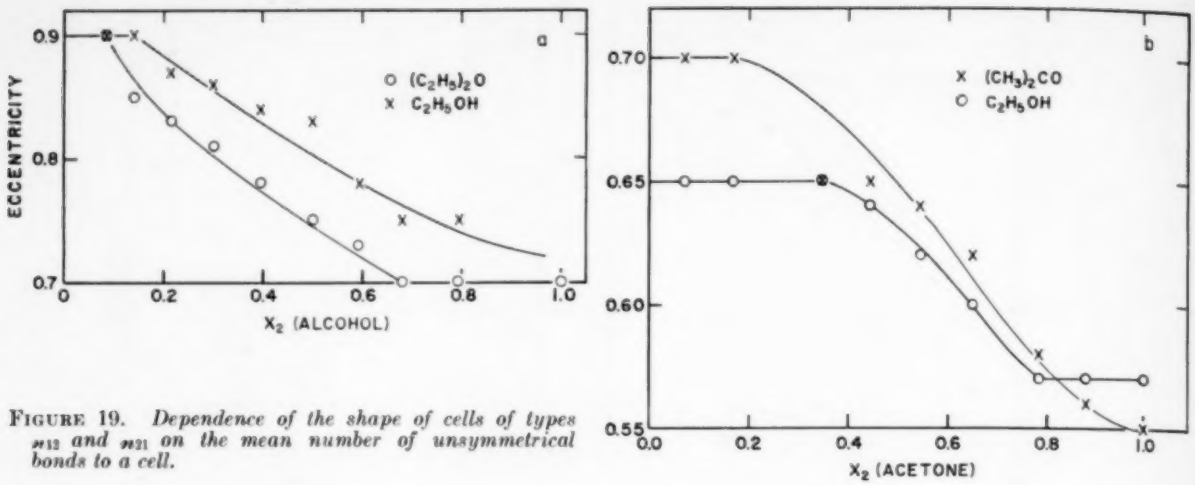

FIGURE 19. *Dependence of the shape of cells of types n_{12} and n_{21} on the mean number of unsymmetrical bonds to a cell.*

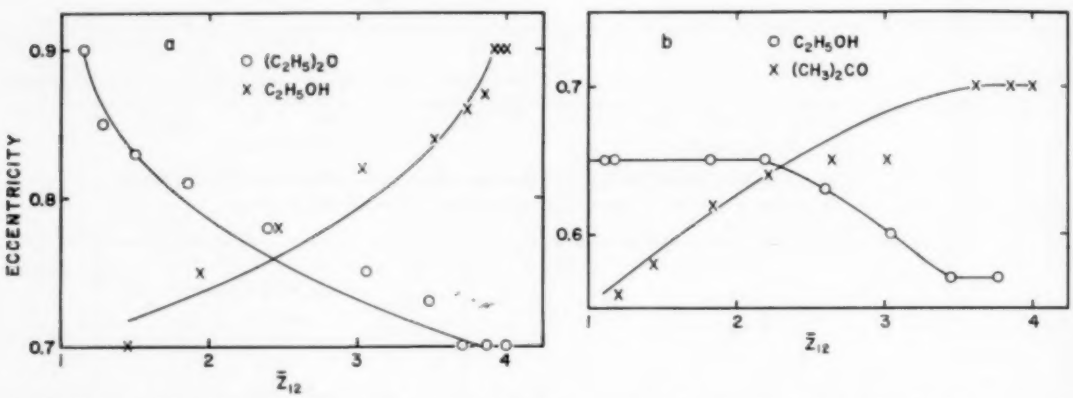

FIGURE 20. *Dependence of the shape of cells of types n_{12} and n_{21} on the mean composition of the mixture.*

in which r_1 and r_{12} are the bond polarizabilities of the symmetrical 1-1 and unsymmetrical 1-2 bonds, respectively, and $\bar{z}_{12}$, the mean number of unsymmetrical bonds to a cell, can take the values 1 to 4. A similar expression holds for the alcohol cells (species 2) with the difference that z is effectively 3 and $\bar{z}_{21}$ can take the values 1 to 3. The polarizabilities of symmetrical bonds at any temperature were determined from the values of R_e given in figure 3.

Characteristic parameters are given in tables 2 and 3. The general results of the calculations are summarized in figures 5 and 6. All molar polarizations have been reduced by an arbitrary factor of 1/4.4. In these figures $\mathscr{P}_{12}^{ideal}$ is the polarization calculated on the assumption that the shape and polarizability of each cell is that of the pure component, $\mathscr{P}_{12}^{exp}$ is the experimental value of the polarization, and $\Delta\mathscr{P}_m = \mathscr{P}_{12}^{exp} - \mathscr{P}_{12}^{ideal}$. The dependence of cell eccentricity on composition is represented in figures 7 and 8.

Curves representing the dependence of $\bar{z}_{12}$, $\frac{\bar{n}_{12}}{\mathscr{N}}$, $\frac{\bar{n}_{12}}{\mathscr{N}_1}$ and $F_1^{(\rho)}$ on x_2 and ρ are given in figures 9 to 12. The corresponding curves for component 2 can be obtained by reflecting these curves in the plane $x_2 = 0.5$.

TABLE 3. *Calculated Parameters*

Substance	δr_{12}	r_{12}	ρ^2-1	$N\overline{\epsilon}_{cell}$
	cm³bond⁻¹mole⁻¹	*cm³bond⁻¹mole⁻¹*		*kcal/mole*
MeOH	(0)	(0.24)	(0)	(0)
H_2O	(0)	(2.24)	(0)	(0)
EtOH	−0.21	1.62	−1	<−4.8
H_2O	−0.62	----------	------	--------
PrOH	−0.28	1.48	−1	<−4.8
H_2O	−0.75	----------	------	--------
t−BuOH	−1.05	1.23	−0.7	−1.44
H_2O	−1.00	----------	------	--------

4.2. Binary Mixtures of Chloroform With Ether and Chloroform With Acetone

On general physical grounds, both mixtures are expected to show evidence of hydrogen bonding. The data are graphically represented in figure 13 and the agreement between $\Delta\mathscr{P}_m^{obs}$ and $\Delta\mathscr{P}_m^{calc}$ is shown in figure 14. Because of the dissimilarity in molecular constitution and structure, the shape of any cell should depend on the composition of its periphery. The variations of the eccentricities with the average number of unsymmetrical bonds and with the composition of the mixture are shown in figures 15 and 16. Selected parameters are given in table 4.

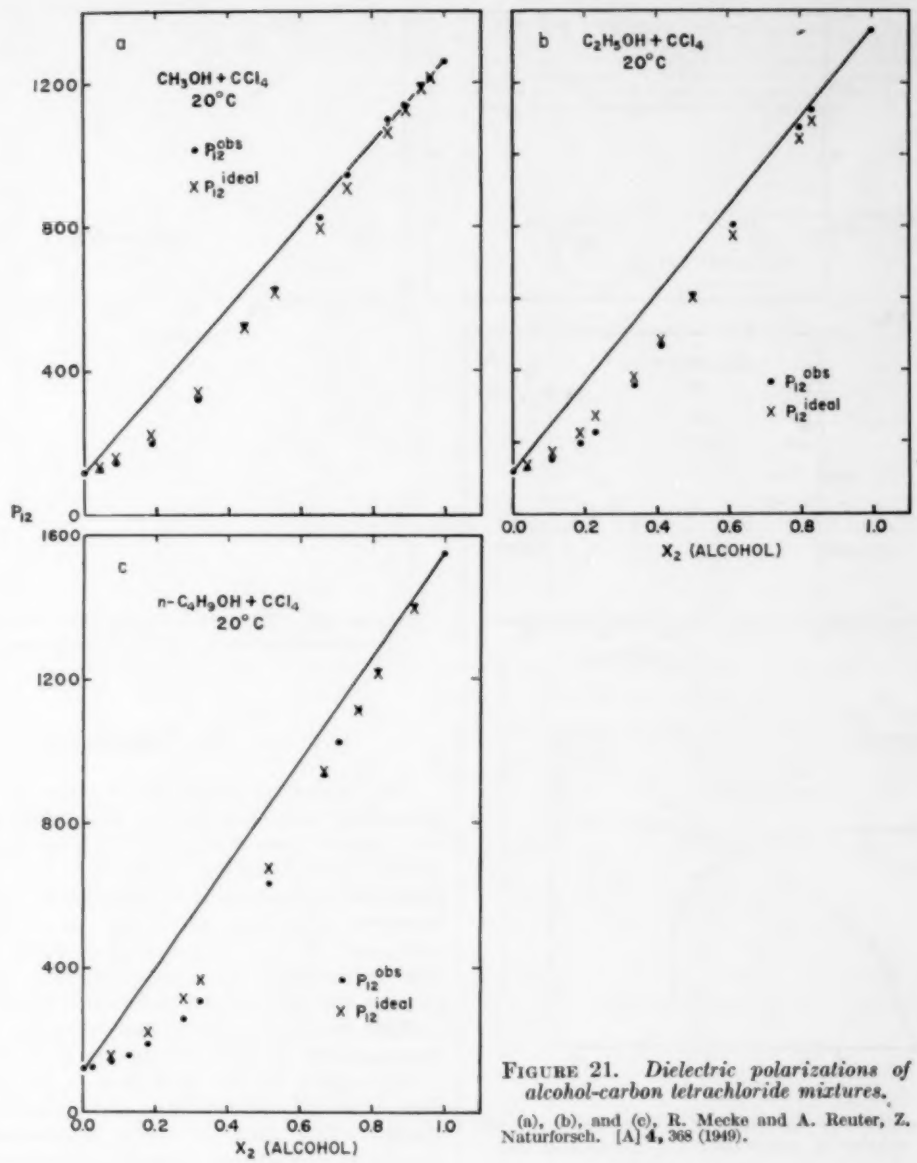

FIGURE 21. *Dielectric polarizations of alcohol-carbon tetrachloride mixtures.*

(a), (b), and (c), R. Mecke and A. Reuter, Z. Naturforsch. [A] **4**, 368 (1949).

The behavior of the systems bromoform-ether and bromoform-isopropyl ether parallels that of the chloroform-ether system.

TABLE 4. *Calculated parameters*

Substance	δr_{12}	r_{12}	ρ^2-1	$N\overline{\epsilon\epsilon}_{cell}$
	$cm^3/ond^{-1}mole^{-1}$	$cm^3/ond^{-1}mole^{-1}$		*kcal/mole*
Chloroform	4	4	−0.90	−2.8
Ether	4	----------	------	--------
Chloroform	1	1	−0.90	−2.8
Acetone	1	----------	------	--------

4.3. Binary Mixtures of Alcohol With Ether and Alcohol With Acetone

For these related mixtures the signs of the polarization of mixing are opposite. The data are graphically represented in figure 17 and the agreement between $\Delta\mathscr{P}_m^{obs}$ and $\Delta\mathscr{P}_m^{calc}$ is shown in figure 18. The parameters selected to reproduce this behavior are given in table 5. In comparison with table 4 these values appear quite reasonable and illustrate the flexibility inherent in the simple electrostatic picture. Variations in the shape of the characteristic cells are shown in figures 19 and 20.

TABLE 5. *Calculated parameters*

Substance	δr_{12}	r_{12}	ρ^2-1	$N\overline{\epsilon\epsilon}_{cell}$
	$cm^3/ond^{-1}mole^{-1}$	$cm^3/ond^{-1}mole^{-1}$		*kcal/mole*
EtOH	3.00	4.80	−0.90	−2.8
Ether	4.80	----------	------	--------
EtOH	−0.7	1.10	−0.50	−0.84
Acetone	1.1	----------	------	--------

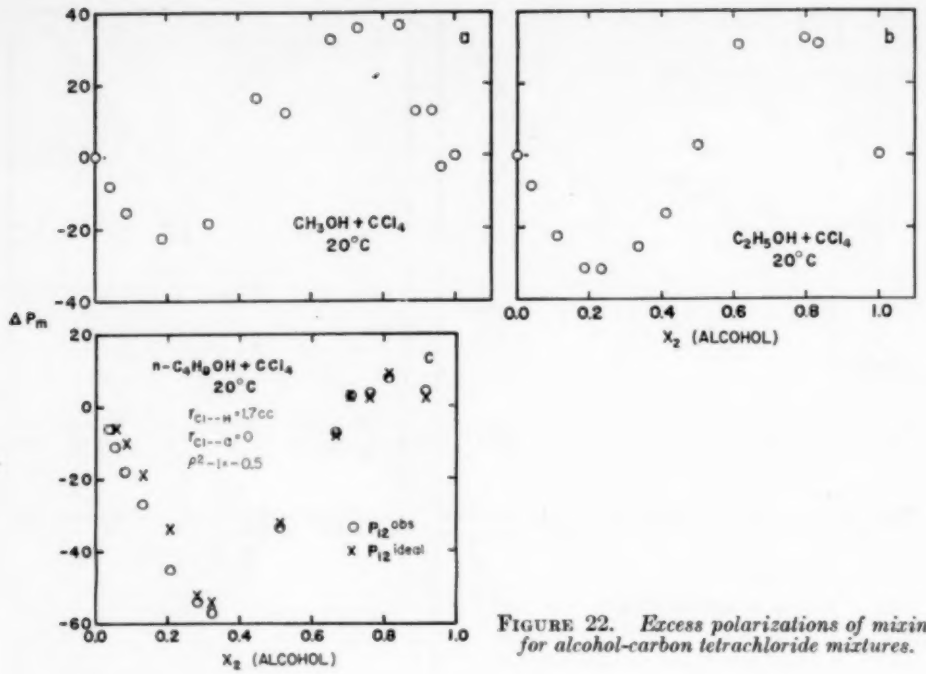

FIGURE 22. *Excess polarizations of mixing for alcohol-carbon tetrachloride mixtures.*

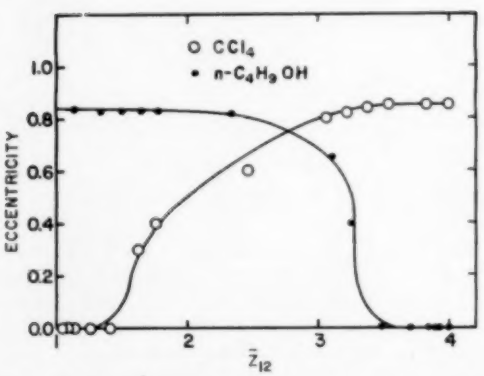

FIGURE 23. *Dependence of the shape of cells of types n_{12} and n_{21} on the mean number of unsymmetrical bonds to a cell.*

4.4. Mixtures of Carbon Tetrachloride and the Simple Alcohols

The behavior of these systems is shown in figures 21 and 22. The system n-C_4H_9OH-CCl_4 is the only one treated in detail. Parameters and their dependence on composition are given in figure 23. The general similarity of the remaining systems suggests that the other mixtures are amenable to the same type of treatment.

4.5. Mixture of Water With Dioxane

This system could be expected to have a behavior somewhat between the water-alcohol systems and the alcohol-ether system. Its behavior is represented in figure 24.

5. Discussion

The principal defect in the theory outlined in the preceding sections lies in the lack of uniqueness of the parameters characterizing a cell. The uncertainty is particularly evident with regard to the parameters of shape and bond polarizability. It appears, however, that the selections made are not unreasonable, and if they are accepted with this reservation, the agreement between theory and experiment can be considered quite satisfactory. In the case of certain mixtures the rather irregular behavior of the eccentricity of the average cell as a function of the composition of the solution is, in part, due to the fact that all calculations were made on the original data. The use of data smoothed to eliminate spurious deviations would undoubtedly improve the regularity in the behavior of this characteristic.

The general utility of the method of analysis described lies in the fact that it offers an independent method for obtaining important information on molecular interactions within liquids. A careful study of a selected series of related mixtures should provide relative values of bond strengths and stabilities of molecular clusters. These quantities may be useful in correlating related macroscopic and molecular properties, such as relative acidity and basicity of groups, mutual solubilities, vapor pressures, and viscostities. Such investigations in which adequate attention has been given to purity of materials and accuracy of measurement are very few.

The bond polarizabilities r_{12}, interaction parameters ρ, and the predominant features of the curve representing the polarization as a function of the composition are summarized in table 6. The results are tentative, and since values and trends may

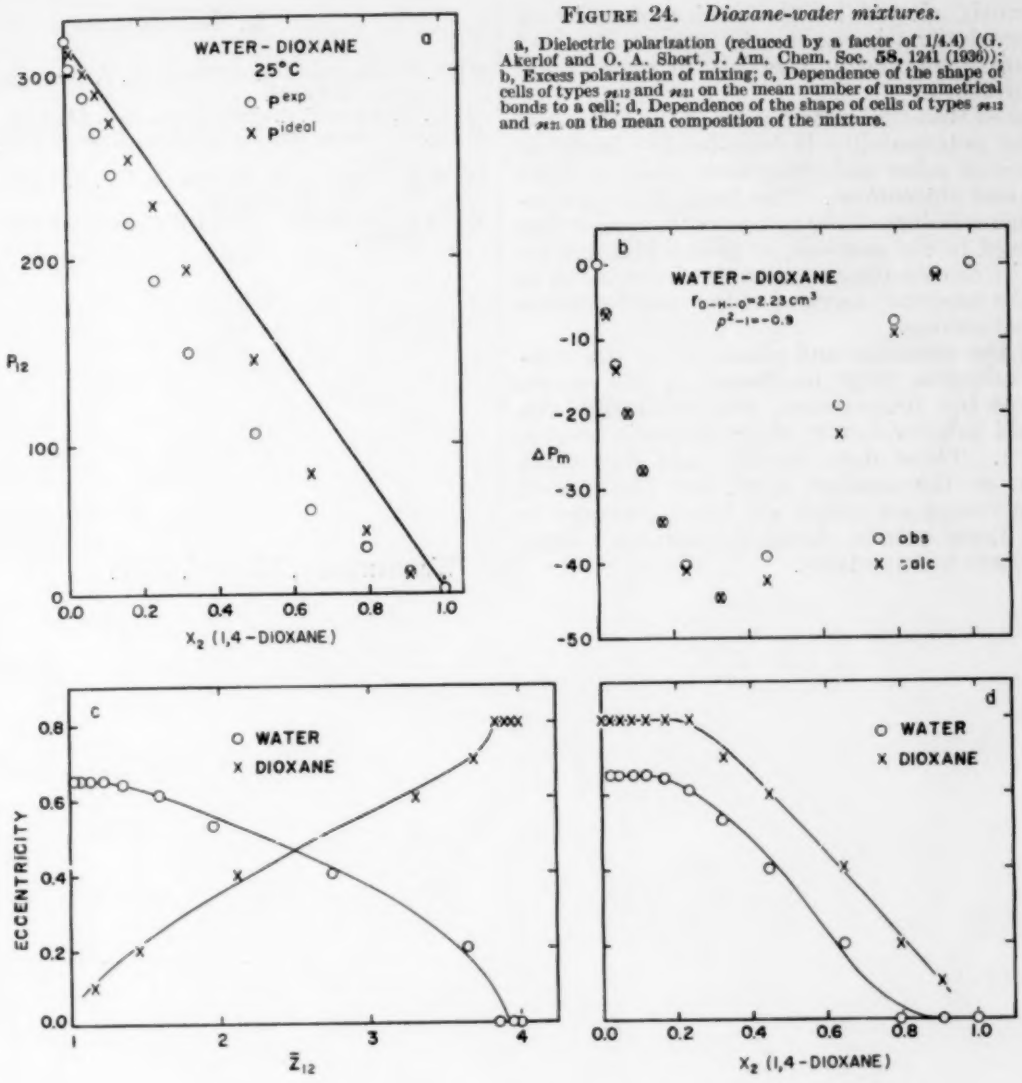

FIGURE 24. *Dioxane-water mixtures.*

a, Dielectric polarization (reduced by a factor of 1/4.4) (G. Akerlof and O. A. Short, J. Am. Chem. Soc. **58**, 1241 (1936)); b, Excess polarization of mixing; c, Dependence of the shape of cells of types $\mathcal{P}_{12}$ and $\mathcal{P}_{11}$ on the mean number of unsymmetrical bonds to a cell; d, Dependence of the shape of cells of types $\mathcal{P}_{12}$ and $\mathcal{P}_{11}$ on the mean composition of the mixture.

TABLE 6. *Summary of cell characteristics*

Type of bond	Mixture	Polarization characteristic	r_{12}	ρ^2-1
			cm³ bond⁻¹ mole⁻¹	
O-H . . . O	Dioxane-water	Minimum	2.23	−0.90
	Methyl alcohol-water	Maximum	2.24	0
	Ethyl alcohol-water	Minimum	1.62	−1
	n-Propyl alcohol-water	Minimum	1.48	−1
	t-Butyl alcohol-water	Minimum	1.23	−0.70
	Ether-ethyl alcohol	Maximum	4.80	−0.90
	Acetone-ethyl alcohol	Minimum	1.10	−0.50
O-H . . . Cl	t-Butyl alcohol-carbon tetrachloride	Maximum and minimum	1.7	−0.50
C-H . . . O	Ether-chloroform	Maximum	4.0	−0.90
	Acetone-chloroform	Maximum	1.0	−0.90

be significantly altered by the choice of different models, speculations based on the results obtained for this limited number and variety of systems are probably premature.

It is noticed that the contribution of the CH . . . O bond to the polarizability is considerably larger in the mixtures of ether and chloroform than in those of acetone and chloroform. This large difference indicates either a failure of the rather crude model that has been used in the analysis, or that additional refinements in the treatment must be introduced in order to take adequate account of the specific nature of bond interactions.

Clues to the existence and character of the complexes in mixtures may be found in the excess (static) dielectric polarization, but conclusive evidence should be provided by their dielectric absorption spectra. These data should yield important information on the number, type, and lifetimes of the various complexes which are often assumed to play a significant role in chemical reactions. Data of this kind are not available.

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WASHINGTON, May 23, 1957.

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